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A SPECTROSCOPIC STUDY OF CALIFORNIA SMOG

Philip L. Hanst, et al

National Environmental Research Center
Research Triangle Park, North Carolina

February 1975

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16. ABSTRACT

Long-path infrared spectroscopy has yielded data on the composition and chemistry of the polluted air at Pasadena, California. Infrared radiation was transmitted along a 417-meter path folded between mirrors in a glass tube 9 meters long. Spectra of polluted air were recorded with a Fourier transform spectrometer system and were plotted in ratio mode against the spectra of humidified reference air. This ratio plotting allowed the observation of weak pollutant absorption lines by removing the background spectrum of water and carbon dioxide lines. Data were taken in late November 1972 and in the summer of 1973. In the 1972 period, the level of auto exhaust pollution was high in the morning and evening, but there was very little formation of ozone and other oxidation products in the air. In the summer of 1973, the morning and evening pollution levels were generally not as high as in the fall, but the stagnation of the daytime air led to the formation and observation of ozone, peroxyacetyl nitrate, formic acid, and other oxidation products. On July 25, a concentration maximum of 0.68 part per million of ozone was recorded, along with maxima of 0.07 part per million of formic acid and 0.05 part per million of peroxyacetyl nitrate. Also measured were hydrocarbons, chlorinated hydrocarbons, carbon monoxide, and methanol. From the spectra, it is concluded that nitric acid vapor was not present in the smog at concentrations higher than 10 parts per billion and ammonia was not present at concentrations higher than 5 parts per billion. The chemistry of the air is discussed in terms of the observations.

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Publication No. EPA-650/4-75-006

ABSTRACT

Long-path infrared spectroscopy has yielded data on the composition and chemistry of the polluted air at Pasadena, California. Infrared radiation was transmitted along a 417-meter path folded between mirrors in a glass tube 9 meters long. Spectra of polluted air were recorded with a Fourier transform spectrometer system and were plotted in ratio mode against the spectra of humidified reference air. This ratio plotting allowed the observation of weak pollutant absorption lines by removing the background spectrum of water and carbon dioxide lines. Data were taken in late November 1972 and in the summer of 1973. In the 1972 period, the level of auto exhaust pollution was high in the morning and evening, but there was very little formation of ozone and other oxidation products in the air. In the summer of 1973, the morning and evening pollution levels were generally not as high as in the fall, but the stagnation of the daytime air led to the formation and observation of ozone, peroxyacetyl nitrate, formic acid, and other oxidation products. On July 25, a concentration maximum of 0.68 part per million of ozone was recorded, along with maxima of 0.07 part per million of formic acid and 0.05 part per million of peroxyacetyl nitrate. Also measured were hydrocarbons, chlorinated hydrocarbons, carbon monoxide, and methanol. From the spectra, it is concluded that nitric acid vapor was not present in the smog at concentrations higher than 10 parts per billion and ammonia was not present at concentrations higher than 5 parts per billion. The chemistry of the air is discussed in terms of the observations.

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CHEMICAL SYMBOLS AND ABBREVIATIONS

CCl_2F_2	Freon 12
CCl_3F	Freon 11
CCl_4	carbon tetrachloride
CH_4	methane
C_2H_2	acetylene
C_2H_4	ethylene
CH_3OH	methanol
C_2HCl_3	trichloroethylene
CH_x	nonmethane paraffinic carbon; x = 2 or 3
CO	carbon monoxide
CO_2	carbon dioxide
HCOOH	formic acid
H_2CO	formaldehyde
HNO_2	nitrous acid
HNO_3	nitric acid
H_2O_2	hydrogen peroxide
NH_3	ammonia
NO	nitric oxide
NO_2	nitrogen dioxide
N_2O	nitrous oxide
N_2O_5	nitrogen pentoxide
O_3	ozone
PAN	peroxyacetyl nitrate
R	hydrocarbon radical

A SPECTROSCOPIC STUDY OF CALIFORNIA SMOG

SUMMARY

Long-path infrared spectroscopy has been applied to the Pasadena atmosphere to obtain data on the chemistry of the smog. A Fourier transform spectrometer and long-path cell were set up on the roof of the Keck Engineering Building at the California Institute of Technology. A folded-path White cell with a base path of 8.7 meters was used. The path was enclosed in a glass tube 9.2 meters long and 0.3 meter in diameter. Forty-four or 48 passes were used, yielding path lengths of 383 and 417 meters. There were two detectors, each at liquid nitrogen temperature: indium antimonide for the frequency region 2000 to 3300 reciprocal centimeters (cm^{-1}), and mercury-cadmium-telluride for the region 700 to 1360 cm^{-1}. The intermediate region was not recorded because of water vapor interference. Spectral resolution was approximately 2 cm^{-1}. The digitized spectra of ambient air were plotted in ratio mode against the spectra of humidified reference atmospheres. This cancelled the water interference, allowing weak pollutant bands to be seen.

Absorption coefficients were carefully ascertained either from the literature or by new measurements. The values used are tabulated and references are given.

The sample was taken in through a 0.1-meter-diameter plastic pipe that ran up into the air 9 meters above the roof of the building. This placed the intake point 27 meters above the ground. The absorption cell could be filled and emptied in just a few minutes. Recording a spectrum took about 5 minutes.

There were two periods of data taking: late November 1972 and July and August 1973. The 1972 period did not include any smoggy days, but it did include mornings and evenings of stationary air, which, although visually clear, showed an accumulation of gaseous pollution. The 1973 summer period included the smog attack of July 24 and 25, which yielded the highest ozone concentrations Pasadena had seen for several years. In the fall, about three spectra per day were recorded; in the summer, 15 to 20 per day were recorded. Spectra are plotted in ratio mode over reference air and also plotted in single-beam mode. A typical spectrum from the fall period shows concentrations approximately as follows: carbon monoxide, 5 parts per million (ppm); methane, 2.5 ppm; paraffinic carbon, 1.0 ppm; acetylene, 0.050 ppm; ethylene, 0.050 ppm.

In the fall mornings and evenings, the carbon monoxide and hydrocarbon levels were about twice as high as in the summer period. Acetylene-to-carbon monoxide ratios were about 1/100 in both periods, but the ratios of paraffinic carbon to carbon monoxide varied, being about 1/4.8 in the fall but only 1/2.6 in the summer. It is suggested that the change in pollution mixture may be the result of air movements, inversion height differences, and temperature differences.

On July 24 and 25, 1973, ozone concentrations reached 0.60 and 0.68 ppm. On those days, carbon monoxide was only about 3 ppm; methane, 2 ppm; and nonmethane hydrocarbon about 1.0 ppm carbon. Acetylene was 0.030 ppm and ethylene only 0.006 ppm, reflecting the trapping of the air mass and the high extent of reaction. Formic acid was identified as the organic reaction product in highest concentration at 0.060 ppm. Peroxyacetyl nitrate (PAN), at 0.050 ppm, was the only identifiable nitrogen-containing product. Also detected were traces of halogenated compounds and methanol. There was a slight indication of hydrogen peroxide with an upper limit of 0.070 ppm. Compounds not detected, and their detection limits, were: nitric acid, 0.010 ppm; methyl nitrate, 0.010 ppm; nitrogen pentoxide, 0.010 ppm; formaldehyde, 0.030 ppm; and ammonia, 0.005 ppm.

Graphs of reactant and product concentrations as functions of time were plotted for several of the smoggy summer days. The general indication

was that the air mass trapped beneath the inversion was well mixed, but had about an 11-hour rate of exchange with the air above it. This slow rate of exchange led to the unusually high degree of reaction and the low ethylene-to-acetylene ratio. Furthermore, it is concluded that the long turnover time for the air mass led to a high degree of conversion of the nitrogen oxides to nitrates, and that by late afternoon most of these nitrates were no longer present either in the gas phase or in the particulate phase.

The high ozone yield and the assumed advanced state of nitrogen oxide conversion indicate that a substantial portion of the hydrocarbon in the air was oxidized by the end of the day.

In addition to the above, other aspects of the photochemistry of the Los Angeles atmosphere are also discussed.

INTRODUCTION

BACKGROUND

The composition of the polluted Los Angeles air has been studied for many years with a variety of measurement methods. The main purpose of direct atmospheric analysis is to determine what people are exposed to, but in addition it can indicate the sources of the pollution, the transformations of the compounds, and the pollution removal paths. The main prior application of long-path infrared absorption to atmospheric analysis was the work of the Franklin Institute group between 1953 and 1957.[1-4] Among the results of that earlier infrared work were the discovery of the peroxyacyl nitrate family of pollutants, the proof of the presence of peroxyacyl nitrates in the Los Angeles atmosphere, and spectroscopic confirmation that ozone is a major product of atmospheric photooxidations.

Infrared techniques were exploited in those earlier studies as fully as the equipment allowed. A prism spectrometer was used, with a thermocouple detector. The folded path was about 240 meters long. Atmospheric spectra were compared to reference spectra by inspection, and point-by-point ratio plots were made through slide-rule calculations. These techniques yielded a limit of pollutant detectability of about 0.05 ppm for peroxyacetyl nitrate, ozone, ethylene, and acetylene. This was sufficient for detection in the ambient air under some conditions, but not all. The limit of detectability for nitric acid, formic acid, and formaldehyde fell in the vicinity of 0.2 ppm--too high for detection. Most of the compounds that were detected by infrared can also be measured with simpler equipment, and therefore long-path infrared studies were relegated to a minor role for the following 15 years.

In the laboratory, the infrared method has continued to be successful. Infrared studies of pollutant reactions at parts-per-million levels have been carried on at the General Motors laboratories and in several university laboratories. These studies have been a major source of progress in air pollution chemistry.[5,6]

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Ambient air analysis has been carried out mainly by the gas chromatographic method. In hydrocarbon analysis, this method easily exceeds the capability of long-path infrared. The infrared method can give a fairly sensitive measure of total hydrocarbons in the air, and a highly sensitive measure of individual hydrocarbon species with one, two, and three carbons, but it cannot resolve the heavier hydrocarbons. Gas chromatography, in contrast, cleanly separates and identifies nearly all components of a mixture of hydrocarbon pollutants, down to parts-per-billion (ppb) levels.

The main value of the infrared method is in identifying and measuring all the assorted nonhydrocarbon species in the air, especially the oxygenated and nitrogenated compounds. This is just the aspect of air analysis in which the chromatographic method is weakest. Thus, the two methods are complementary, and long-path infrared methodology still has a vital role to fill in atmospheric studies.

Improved optical components of many different types have been developed in the past 20 years. These include the solid-state detectors, the laser, the scanning Michelson interferometer, and the dedicated minicomputer for processing interferograms and spectra. The Fourier transform spectrometer systems now commercially available bring all of these components together in a package that yields higher resolution and higher signal-to-noise ratios than conventional grating or prism spectrometers. Furthermore, the new spectrometer data systems permit the automatic plotting of ratio spectra when a single absorption cell is used.

Since new instrumental improvements were capable of yielding a 10-fold or even 100-fold increase in measurement sensitivity in an atmospheric long-path infrared experiment, a new long-path absorption cell has been built especially for use with a Fourier transform spectrometer. It was soon demonstrated that the combination was yielding a parts-per-billion detection sensitivity for many of the important air pollutant species. These results were described in a recently published article, which should be consulted for additional details.[7]

EQUIPMENT AND METHOD

In 1972, as part of a study of particulate and gaseous pollution, the Fourier transform spectrometer and long-path cell were set up in Pasadena on the roof of the Keck Engineering Building at the California Institute of Technology. A folded-path White cell with a base path of 8.7 meters was used.[8] The path was enclosed in a glass tube 9.2 meters long and 0.3 meter in diameter. The tube is shown in Figure 1. Either 44 or 48 passes

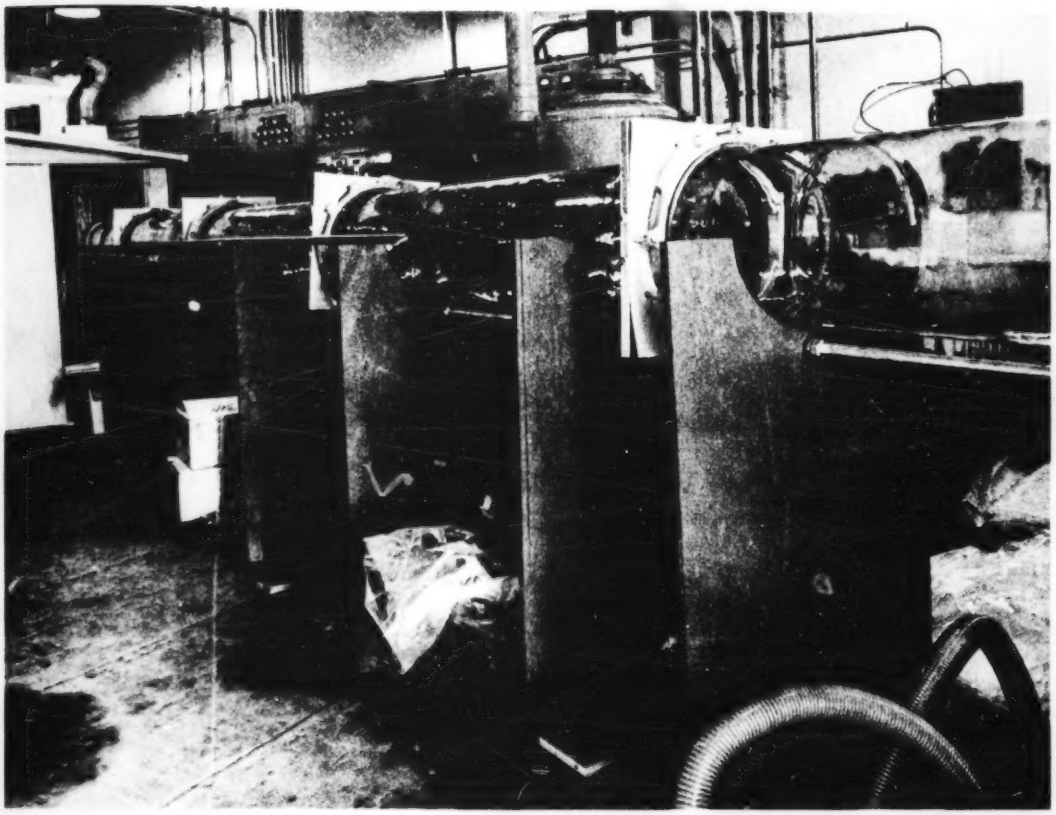

Figure 1. Glass tube in penthouse.

were used, yielding path lengths of 383 and 417 meters. The only place available to locate the system was inside the penthouse for the air conditioning and heating machinery of the building. Although this proved to be a shaky and noisy environment, most of the vibration was eliminated by shock mounts placed under the tube and the spectrometer. The spectrometer and its data system were housed in a small air-conditioned shed, as shown in Figure 2. Two detectors were used, each at liquid nitrogen temperature:

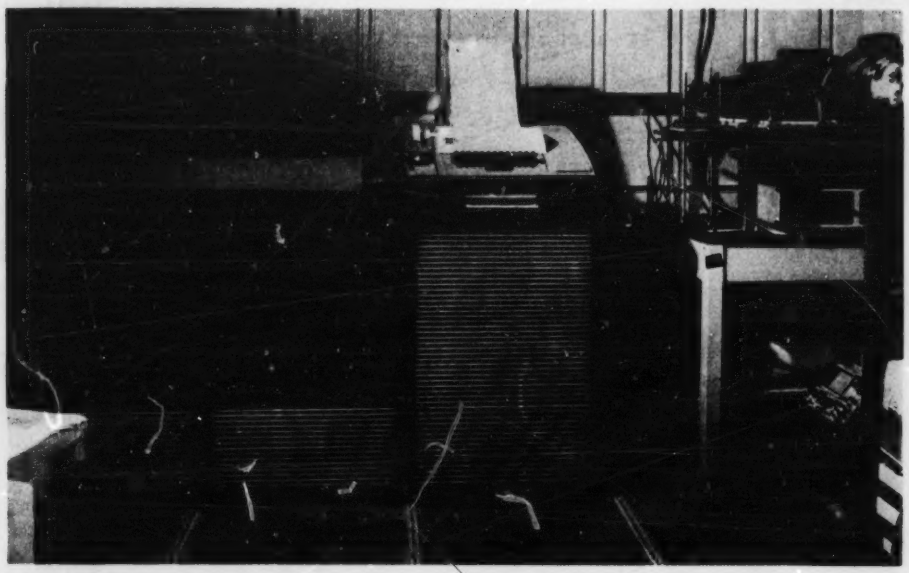

Figure 2. Spectrometer and data system in shed.

indium antimonide for the frequency region 2000 to 3300 cm^{-1}, and mercury-cadmium-telluride for the region 700 to 1360 cm^{-1}. The region 1360 to 2000 cm^{-1} was not recorded because of water vapor interference.

The system components are diagrammed in Figure 3. Infrared radiation

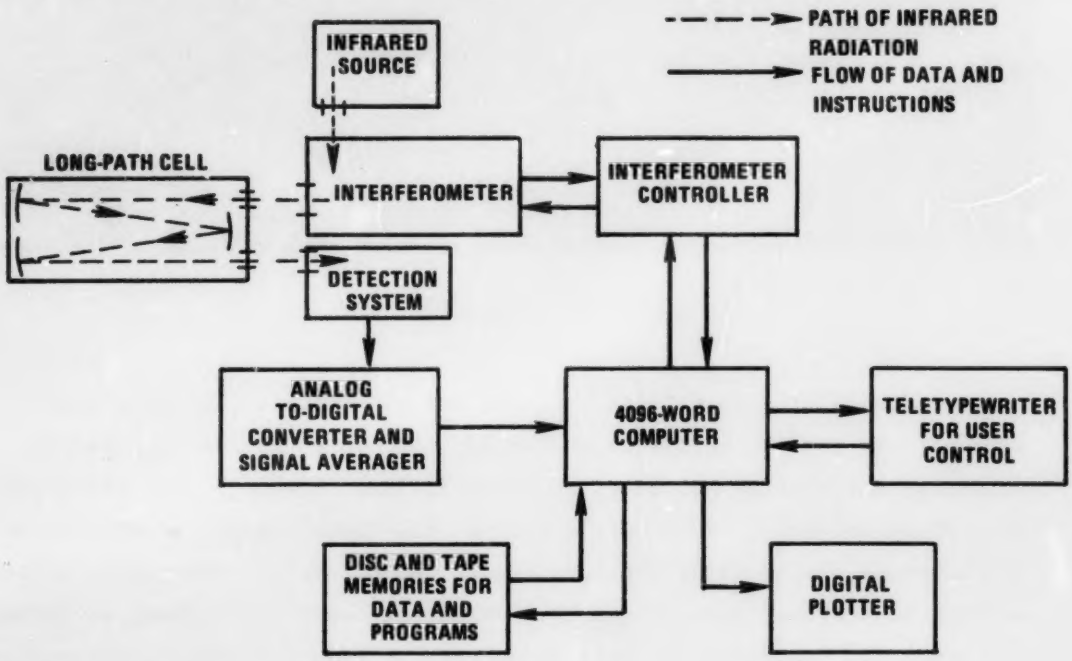

Figure 3. Pollutant measuring system.

from a Nernst glower source was projected into the interferometer. The modulated optical output of the interferometer (the interferogram) was passed through the long absorption cell to the detector. Forty digitized recordings of each interferogram were added together in the data system in order to increase the signal-to-noise ratio. The summed interferogram was then transformed to yield the spectrum. (Spectral resolution was approximately 2 cm^{-1}.) The digitized spectrum could be displayed, or it could be stored in the computer memory for future access. Generally, the ratio between the air spectrum and a stored reference spectrum was computed and plotted.

The air sample was taken in through a 0.1-meter-diameter plastic pipe, which ran out the door of the penthouse and up into the air about 9 meters above the roof on the fourth floor. This placed the intake point about 27 meters above the street. A blower kept the air moving through the intake pipe at all times. The glass long-path cell was evacuable down to less than 1 torr pressure. The manner of collecting a sample was as follows: (1) The long-path cell was evacuated. (2) By opening a valve, the flow of outside air was directed into the long-path cell so that the cell was filled to a pressure sufficient to cancel the water vapor lines against those in a reference spectrum. Generally, the pressure was between 500 and 600 torrs. (3) Recording of the spectrum was begun immediately and was completed within about 5 minutes. It is hard to imagine that this manner of sampling could result in the loss of any labile species of molecules in the air. The residence time of the air sample in the intake pipe was no more than a few seconds, and in the glass cell it was no more than a few minutes. There was good agreement between the values of ozone measured by infrared and the values measured by chemiluminescence instruments.

The reference air samples were made up from tank air, humidified to match the water content of the ambient air. Humidity was adjusted by mixing two portions of reference air in the long-path cell. One portion came straight from the tank, dry. The other came from a reservoir of tank air stored in a large plastic bag with liquid water. The work done in late November 1972 used Matheson Zero Air for reference. This turned out to be nearly devoid of carbon dioxide but to contain about 1 ppm of carbon monoxide. The absence of carbon dioxide was a disadvantage

because it allowed atmospheric carbon dioxide to show in the ratio plots. The presence of carbon monoxide was also a disadvantage because it cancelled some of the absorption by ambient carbon monoxide pollution, thus requiring a correction factor. The 1973 work used Scott reference air to which 300 ppm of carbon dioxide had been added. This cancelled most of the carbon dioxide in the ratio plots, but not all. The Scott air also turned out to include about 1 ppm of carbon monoxide. It did not prove feasible to obtain an exact water balance in all cases; but, generally, at least 90 percent of the water interference was removed.

CALIBRATION SPECTRA

Incorrect absorption coefficients are the most likely source of error in atmospheric infrared studies. Many of the molecular species detected and measured in this work do not have well-documented reference spectra. Published absorption coefficients must be used with caution because of the many possible sources of error in handling the gas and in recording and interpreting the spectra. Whenever possible, absorption coefficients to be used were rechecked by running new reference spectra on samples at parts-per-million concentrations in a laboratory long-path cell. The simplest and safest cases of absorption coefficient measurement involve the large polyatomic molecules, which are thermally stable. This includes, for example, paraffinic hydrocarbons, alkyl nitrates, ketones, alcohols, and aldehydes with two or more carbons. The spectra in these cases have so many overlapping lines that there is no inherent fine structure in the bands at atmospheric pressure. The absorption coefficient is therefore independent of pressure and instrumental resolution; the absorption equation is obeyed at all absorptivities. The most difficult cases involve the molecules with a small number of lines in their spectra, such as carbon monoxide, nitric oxide, and hydrogen chloride. The apparent absorption coefficients in these cases are dependent on total pressure, concentration of the absorbing species (because of self-broadening), and instrumental resolution. The absorption equation is only obeyed at small absorptivities. Thermally unstable species, such as ozone and hydrogen peroxide, and species that adsorb or polymerize, such as formic acid and formaldehyde, have their own

characteristic measurement difficulties. For these reasons, a listing of absorption coefficients and the conditions under which they were obtained is given in Table 1.[7, 9-12] Reference spectra with sharp bands or lines were measured with resolution similar to that used in recording the atmospheric spectra. The values of the absorption coefficient, κ, are those used in the absorption equation:

$$\ln (I_o/I) = \kappa PL$$

where:

$\ln$ = natural logarithm

I_o = incident intensity of infrared frequency specified

I = transmitted intensity

P = partial pressure of component, atm

L = optical path length, cm

κ = absorption coefficient, cm^{-1} atm^{-1}

For proper calibration of carbon monoxide measurements, it was necessary to measure the absorption coefficient as a function of the apparent energy ratio at the chosen point in the spectrum. A range of concentration of carbon monoxide between 9 and 0.5 ppm was used. The results are plotted in Figure 4. The absorption coefficient values for carbon monoxide were found to be about one-half as great as they were found to be in a similar measurement made at torr-level concentrations in a 10-cm absorption cell.[9] The difference is probably due to self-broadening of the lines.

Table 1. ABSORPTION COEFFICIENTS

Pollutant	Measurement frequency, cm^{-1}	Absorption coefficient, $cm^{-1}\ atm^{-1}$	References and comments
Acetylene (C_2H_2)	720	180	Present work; measured at parts-per-million concentration in air
Ammonia (NH_3)	930 967	27 35	Present work
Carbon monoxide (CO)	2170	See curve in Figure 4	Present work; spectra of parts-per-million concentrations of CO in 600-torr air were recorded in the long-path cell at a resolution similar to that used in Pasadena
Carbon tetrachloride (CCl_4)	793	210	Reference 10
Ethylene (C_2H_4)	950	20	Present work; measured at parts-per-million concentrations in air
Formaldehyde (H_2CO)	2780	10	Present work
Formic acid (HCOOH)	1105	13	Applies to central peak only; measured at parts-per-million concentration in long-path cell
Freon 12 (CCl_2F_2)	921	45	Reference 10
Hydrogen peroxide (H_2O_2)	1250	9 ± 3	Present work
Methane (CH_4)	3017 1307	12 11	Reference 9; rechecked in present work with 1.7 ppm CH_4 in atm of air
Methanol (CH_3OH)	1033	25	Present work
Methyl nitrate (CH_3ONO_2)	853 1018 1290	30 18 35	Present work
Nitric acid (HNO_3)	896	20	Reference 7
Nitrogen Pentoxide (N_2O_5)	740 1248	40 40	Present work
Ozone (O_3)	1053	8.6	Reference 11
Nonmethane paraffinic carbon (CH_x)[a]	2970	4.0	An average of the absorption coefficient values, per carbon, calculated for propane, butane, pentane, and hexane from Reference 9
Peroxyacetyl nitrate (PAN)	1162	32	Reference 12
Trichloroethylene (C_2HCl_3)	852	22	Reference 10

[a] Does not include methane or the ring carbons in aromatics; thus, the subscript x indicates two or three hydrogens, but not one or four.

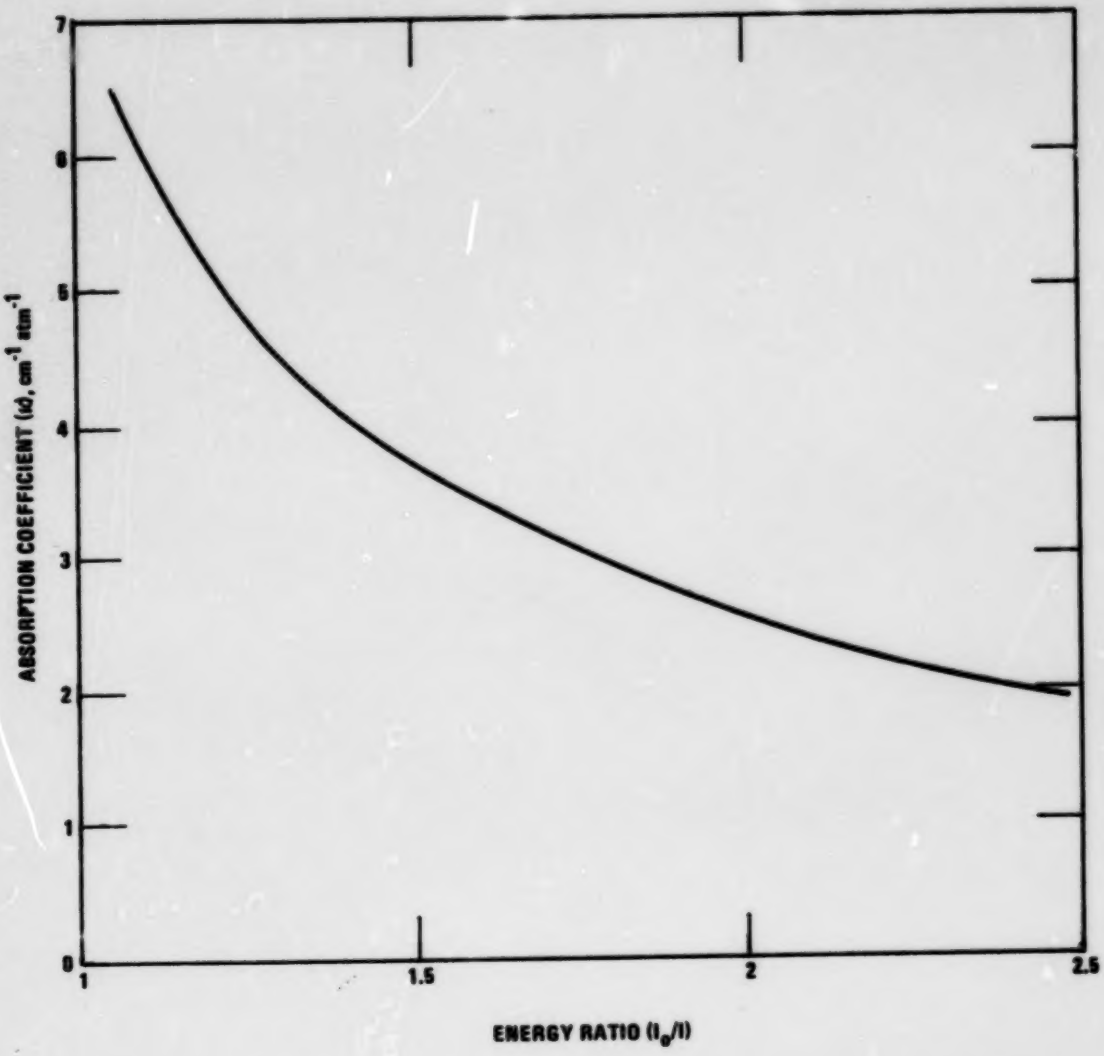

Figure 4. Carbon monoxide absorption coefficient as a function of apparent energy ratio at 2700 cm^{-1}.

RESULTS AND DISCUSSION

RESULTS

There were two periods of data taking: (1) late November 1972 and (2) July and August 1973. The 1972 period did not include any smoggy days, but it did include mornings and evenings of stationary air that, although visually clear, showed an accumulation of gaseous pollution. The 1973 summer period included the smog attack of July 24 and 25, which yielded the highest ozone concentrations Pasadena had seen for several years.

A sample spectrum from the late November period is shown in Figure 5. This spectrum was obtained on Thursday evening, November 30, 1972, at 5:15 p.m. Sample pressure was 760 torr, and the path length was 383 meters. Only the higher frequency end of the spectrum recorded with the indium antimonide detector is shown. In interpreting this spectrum, it should be recognized that approximately 10 percent of the signal was due to stray radiation that travelled only a few tens of meters in the cell, rather than the full path. This condition could have been corrected but was not recognized in time. When properly allowed for, the stray radiation does not invalidate any of the results. The single-beam atmospheric absorption spectrum appears in the lower part of the figure, and the ratio plot of that spectrum over the spectrum of humidified reference air appears in the upper part. The single-beam plot shows the many water vapor lines, which are removed in the ratio plot. In proceeding from lower frequency to higher, the single-beam spectrum shows a gradual decrease in signal due to the response characteristics of the detection system. The ripples

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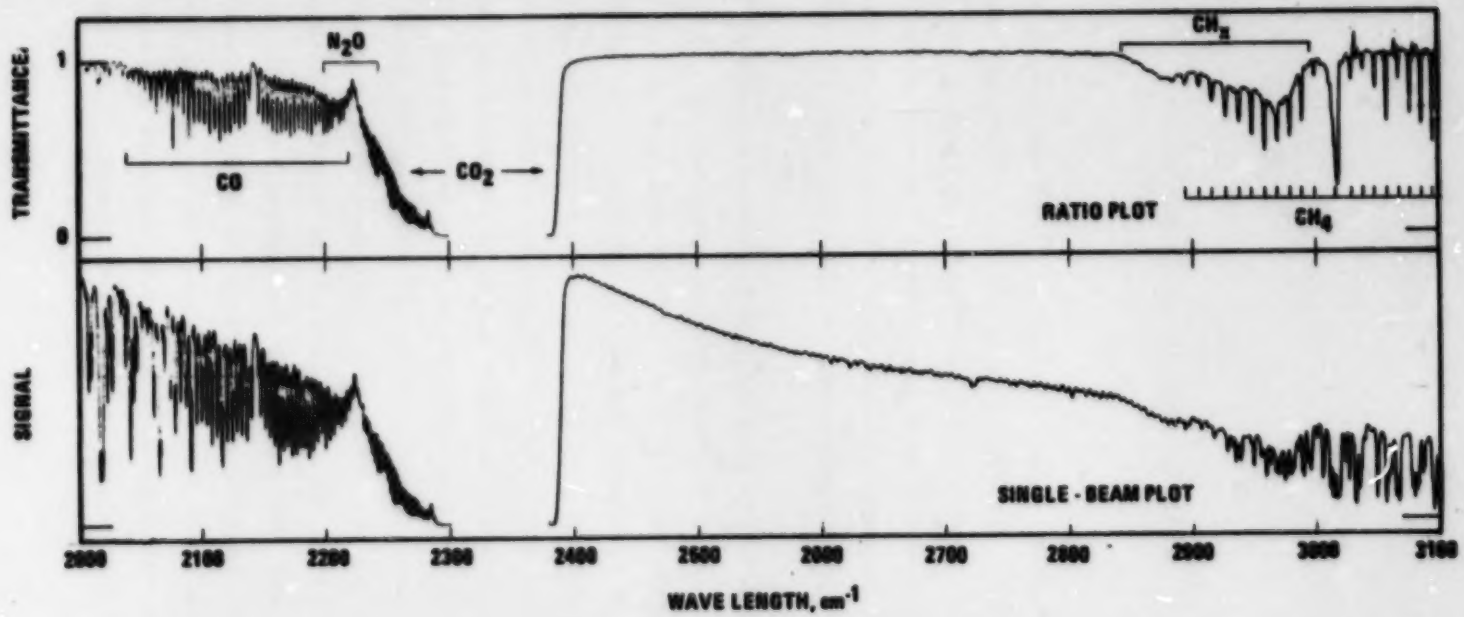

Figure 5. Atmospheric spectrum, November 30, 1972, 5:15 p.m. Path, 383 meters; pressure, 760 torr; detector, indium antimonide.

in the single-beam plot, which are especially evident between 2400 and 2500 cm^{-1}, are the result of interference phenomena in the train of optical components. The ripples are cancelled out in the ratio plot. A slight overcompensation of the water vapor absorption has driven some of the strong water lines above unity in the ratio plot. The Matheson Zero Air used for reference contained about 1 ppm of carbon monoxide, but no carbon dioxide, nitrous oxide, or methane. The carbon monoxide band in the ratio plot is therefore smaller than it should be, but the other bands appear at full strength. Concentrations of pollutants calculated from the spectrum are carbon monoxide, 11.5 ppm; methane, 2.8 ppm; non-methane paraffinic carbon atoms (CH_x), 2.2 ppm. Nitrous oxide was at its normal value of 0.25 ppm.[13] Carbon dioxide was not calculated from the spectrum. There was no indication of formaldehyde.

Spectra from July 25, 1973, covering the region 700 to 1360 cm^{-1} are shown in Figures 6 and 7. Stray light in these cases was probably less than 5 percent. For these spectra, the mercury-cadmium-telluride detector was used. In the 9:30 a.m. spectrum, Figure 6, the sample pressure was 600 torr, and the path length 417 meters. The lower spectrum is the single-beam plot, showing mainly water and carbon dioxide bands. The middle spectrum is a ratio plot using a reference spectrum of Scott tank air properly humidified to cancel nearly all of the water vapor absorption. This air also contained about 300 ppm of carbon dioxide, which cancelled about 90 percent of the carbon dioxide absorption. The reference air did not contain methane or other hydrocarbons. The upper spectrum in the figure is a scale-expanded plot of the spectral region 800 to 1200 cm^{-1} in which the ordinate scale is 19 times larger than in the center spectrum. Marked on the spectra are absorption bands for the following compounds and concentrations: ozone, 0.09 ppm; peroxyacetyl nitrate, 0.016 ppm; methanol, 0.015 ppm; Freon 12, 0.008 ppm; trichloroethylene, 0.015 ppm (perhaps underlaid with some absorption by Freon 11); formic acid, 0.020 ppm (underlaid with some absorption by Freon 12); acetylene, 0.028 ppm; ethylene, 0.015 ppm (distorted by a noise spike); and methane, 2.0 ppm.

In the 1:00 p.m. spectra, Figure 7, we see that the photochemical reaction products--ozone, formic acid, and peroxyacetyl nitrate--have increased substantially. In Figure 7, the expansion factor of the upper

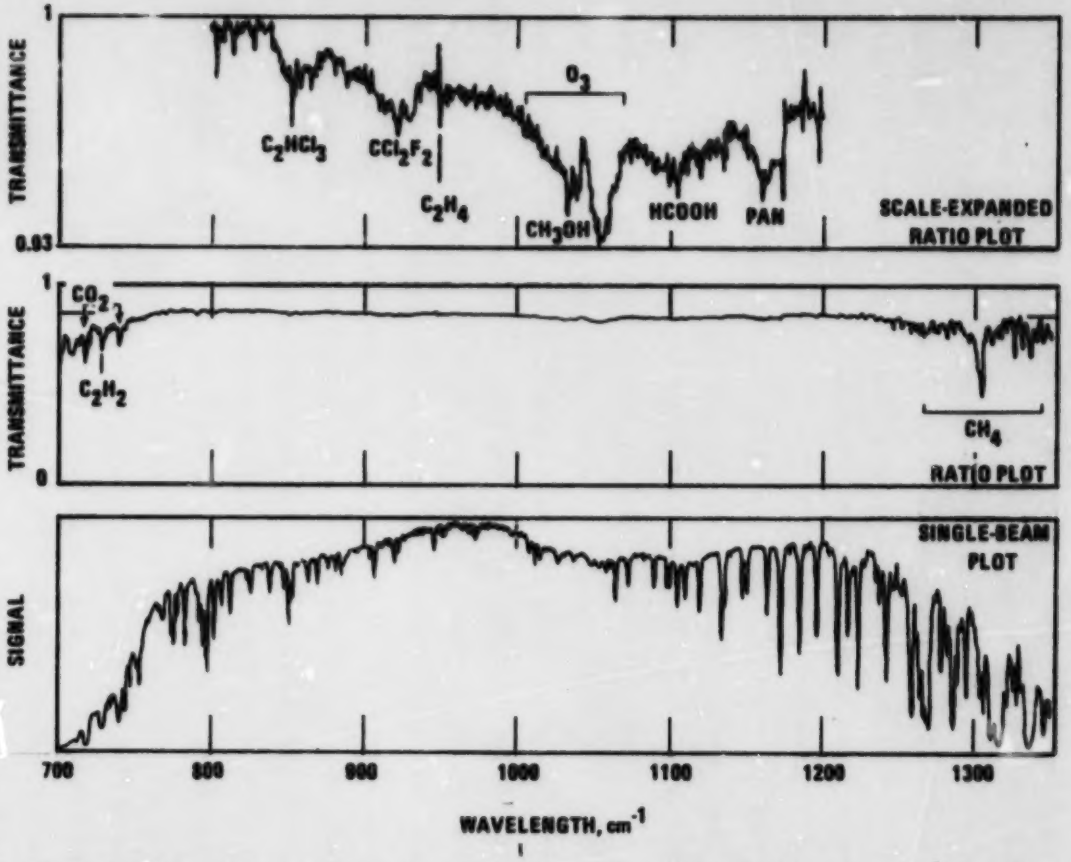

Figure 6. Atmospheric spectrum, July 25, 1973, 9:30 a.m. Path, 417 meters; pressure, 600 torr; detector, mercury-cadmium-telluride.

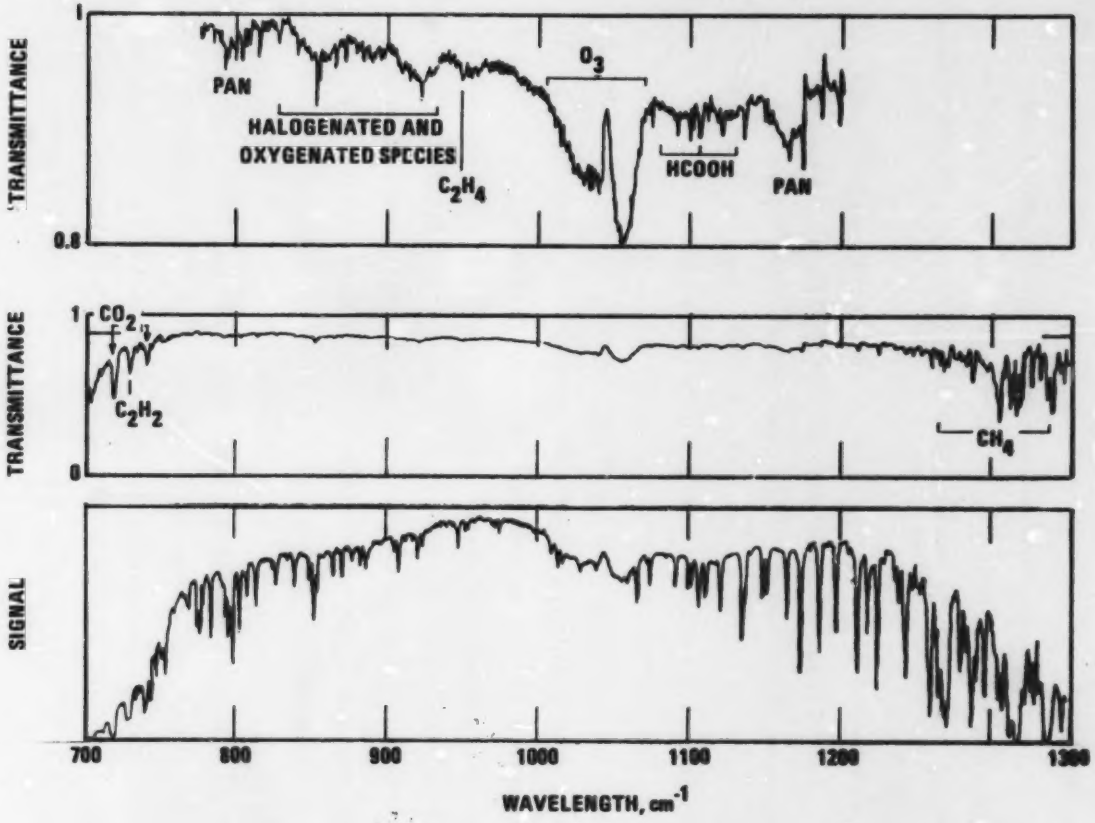

Figure 7. Atmospheric spectrum, July 25, 1973, 1:00 p.m. Path, 417 meters; pressure, 535 torr; detector, mercury-cadmium-telluride.

spectrum is only 7-fold. The 1:00 p.m. values were ozone, 0.60 ppm; formic acid, 0.063 ppm; and peroxyacetyl nitrate, 0.051 ppm. By 1:00 p.m. the acetylene and methane had increased slightly to values of 0.030 ppm and 2.4 ppm, respectively. The ethylene concentration had decreased to approximately 0.009 ppm.

Pollutant concentrations measured between November 20, 1972, and December 1, 1972, are listed in Table 2. In general, this was a time of air stagnation morning and evening, ventilation and clean air in the middle of the day, and no smog.

Concentrations measured on selected days in the summer of 1973 are listed in Table 3. July 24 and 25 were days of very high ozone concentration, and all values calculated from the spectra of those days are listed. July 26 was also expected to be a day of very high oxidant, and in fact, Federal employees in the Los Angeles area were excused from work. However, the atmospheric conditions changed--perhaps beginning in the late afternoon of the 25th--and very little smog developed. Other days of high ozone showed a pattern of concentrations and variations with time generally similar to those observed on the smoggy days of July 24 and 25. Since the ratio of nonmethane paraffinic hydrocarbon to carbon monoxide can indicate pollutant sources, the values for those two pollutants measured on 5 days in August are also listed. The gaps in the table result from the choice of detectors and spectral regions for recording. The bulk of the July 24 data was obtained in the 700- to 1400-cm^{-1} region, using the mercury-cadmium-telluride detector; hence, they do not show carbon monoxide or paraffinic carbon. On July 25 and 26, the data obtained with the mercury-cadmium-telluride detector were recorded out to 2300 cm^{-1} and hence include carbon monoxide. The various measurements that show paraffinic carbon and carbon monoxide were obtained with the indium antimonide detector. Some additional details from the spectra will be included in the following discussions.

DATA ANALYSIS AND DISCUSSION

Analysis of the results yields information on the sources and sinks of the pollutants and on the pollutant transformations in the air. The

Table 2. POLLUTANT CONCENTRATIONS (ppm), PASADENA, 27 meters ABOVE GROUND, NOVEMBER 20-DECEMBER 1, 1972[a]

Date and time	Carbon monoxide	Methane	Nonmethane paraffinic carbon	Acetylene	Ethylene
Nov. 20-11:30 a.m.	1.2	2.1	0.16	0.011	0.010
20- 4:45 p.m.	3.4	2.2	0.45		
21-11:00 a.m.	1.2	1.9	0.11	0.017	0.010
21- 4:10 p.m.	2.7	2.3	0.29	0.030	0.025
22- 8:10 a.m.	7.5	2.8	1.23	0.083	0.098
22-12:00 a.m.	3.1	2.3	0.34	0.022	0.026
27- 8:10 a.m.	9.5	2.7	1.42	0.090	0.071
27- 3:10 p.m.	4.8	2.5	0.89	0.041	0.030
27- 5:00 p.m.	6.0	2.6	1.34	0.043	0.042
28- 9:00 a.m.	4.0	2.4	0.45	0.030	0.030
28- 3:30 p.m.	3.6	2.6	0.63	0.039	0.020
28- 5:00 p.m.				0.058	0.046
29-10:00 a.m.	2.6	2.2	0.30	0.019	0.015
29- 3:15 p.m.	0.9	2.0	0.16	0.006	0.005
30- 8:10 a.m.	6.1	2.2	1.2	0.044	0.045
30- 1:10 p.m.	1.8	2.2	0.42	0.022	0.015
30- 5:15 p.m.	11.5	2.8	2.2	0.071	0.065
Dec. 1- 8:15 a.m.	11.2	2.7	2.0	0.090	0.092
1- 4:00 p.m.	5.6	2.6	1.25	0.041	0.031

[a]Blanks indicate no measurement.

Table 3. POLLUTANT CONCENTRATIONS (ppm), PASADENA, 27 meters ABOVE THE GROUND, SUMMER 1973[a]

Date and time	Carbon monoxide	Methane	Nonmethane paraffinic carbon	Acetylene	Ethylene	Ozone	Formic acid	Peroxy acetyl nitrate
July 24-10:00 a.m.		2.0		0.022	0.014	0.07	0.017	0.011
10:30 a.m.		1.9		0.025	0.012	0.10	0.020	0.013
11:00 a.m.		1.9		0.024	0.012	0.13	0.027	0.016
11:30 a.m.		1.9		0.021	0.005	0.22	0.031	0.026
12:00 noon		1.9		0.019	0.005	0.25	0.030	0.025
12:30 p.m.		2.2		0.019	0.005	0.26	0.031	0.038
1:00 p.m.		2.3		0.026	0.004	0.35	0.033	0.029
1:30 p.m.		2.3		0.029	0.004	0.41	0.038	0.035
2:00 p.m.		2.2		0.024	0.005	0.57	0.048	0.041
2:30 p.m.		2.1		0.033	0.005	0.59	0.057	0.047
3:00 p.m.		2.1		0.036	0.005	0.57	0.053	0.047
3:30 p.m.		1.9		0.033	0.005	0.46	0.047	0.036
4:10 p.m.	3.3		0.71					
July 25- 7:10 a.m.	2.2		0.78					
8:00 a.m.	2.4	2.0	1.05	0.023	0.018	—	0.013	0.004
9:30 a.m.	2.1	2.0		0.028	0.015	0.09	0.020	0.016
10:00 a.m.	2.1	2.0		0.026	0.015	0.19	0.038	0.019
10:30 a.m.	2.6	2.0		0.026	0.009	0.25	0.043	0.022
11:00 a.m.	2.8	2.1		0.022	0.009	0.32	0.060	0.037
11:30 a.m.	2.8	2.2		0.025	0.007	0.37	0.064	0.034
12:00 noon	2.6	2.2		0.024	0.006	0.39	0.054	0.033
12:30 p.m.	2.9	2.2		0.024	0.007	0.42	0.057	0.040
1:00 p.m.	3.9	2.4		0.030	0.009	0.60	0.063	0.051
1:30 p.m.	3.9	2.4		0.032	0.010	0.68	0.072	0.051
2:00 p.m.	3.5	2.4		0.036	0.011	0.66	0.068	0.053
2:30 p.m.	2.9	2.3		0.031	0.009	0.59	0.063	0.044
3:00 p.m.	2.8	2.3		0.025	0.006	0.53	0.064	0.046
3:30 p.m.	2.5	2.2		0.019	0.005	0.45	0.057	0.043
4:00 p.m.	2.1	2.0		0.014	0.004	0.35	0.055	0.034
4:30 p.m.	2.2		0.49					
July 26- 8:10 a.m.	2.5		1.1					
9:30 a.m.	2.0	2.0		0.022	0.015	0.06	0.010	0.009
10:00 a.m.	1.5	2.0		0.020	0.016	0.12	0.010	0.010
10:30 a.m.	1.8	2.1		0.022	0.015	—	—	—
11:00 a.m.	1.9	2.1		0.024	0.013	0.05	0.005	0.005
11:30 a.m.	1.8	2.0		0.020	0.010	0.04	—	—
12:00 noon	1.5	1.8		0.017	0.006	0.05	—	—
12:30 p.m.	1.5	1.8		0.013	0.004	0.05	—	—
3:05 p.m.	1.6		0.67					
Aug. 8 - 4:30 p.m.	1.7		0.44					
9 - 8:00 a.m.	2.5		0.75					
3:00 p.m.	2.2		0.61					
22 - 3:00 p.m.	2.1		0.60					
23 -10:00 a.m.	1.3		0.36					
24 -11:30 a.m.	1.3		0.51					

[a]Blanks indicate no measurement. Dashes indicate not detected.

data will be discussed in terms of (1) the ratios of pollutant concentrations, (2) the time variations of the concentrations, (3) the amounts of the pollutants seen or not seen, and finally, (4) the material balance (or unbalance) in the photochemically reacted air.

Ratios of Pollutant Concentrations

Plots have been made of the pairs of acetylene and carbon monoxide values for the separate fall and summer periods. These are shown in Figure 8. The fall data are from Table 2 for 8 days between November

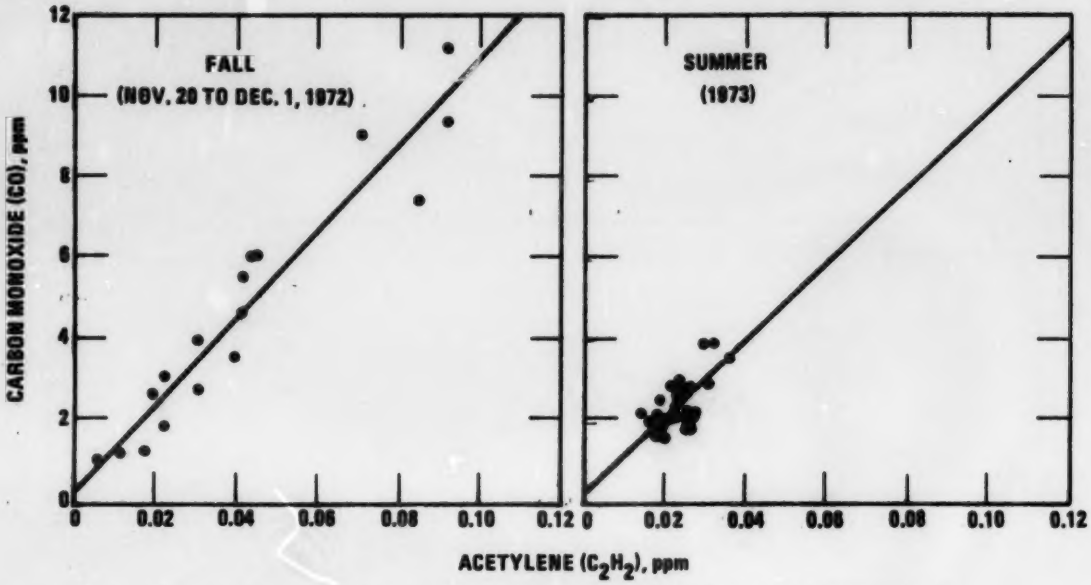

Figure 8. Acetylene versus carbon monoxide, fall and summer periods.

20 and December 1, 1972. The summer data, from Table 3, apply to July 25 and 26 and August 9, 1973. The ratios indicated by the lines drawn through the points are about 0.009 in each case. This ratio is typical of auto exhaust, which is thus indicated as the principal source of both pollutants during both periods. Acetylene and carbon monoxide each are low in photochemical reactivity, and it can be assumed that they did not undergo oxidation between the time of emission into the air and the time of the measurements.

Plots of carbon monoxide concentrations against the concentrations

of nonmethane paraffinic hydrocarbons, as indicated by the C-H absorption band at 2970 cm^{-1}, are given in Figure 9. These plots show ratios that

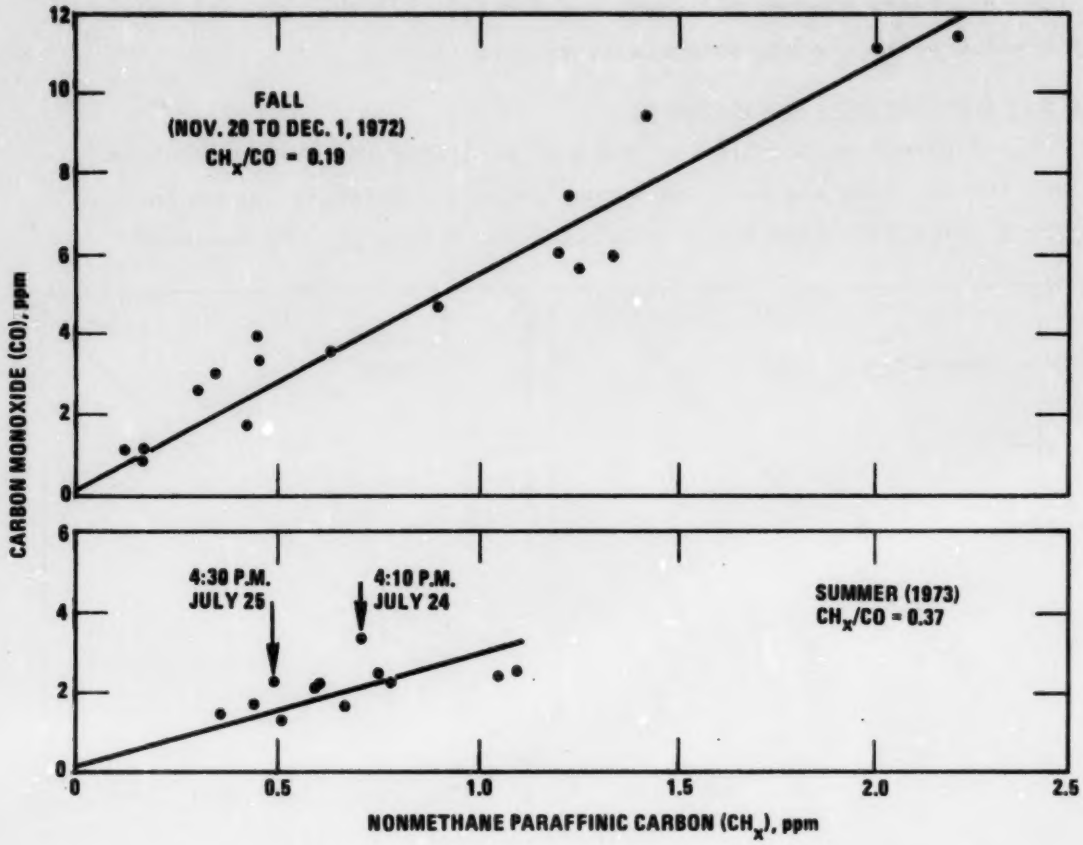

Figure 9. Nonmethane paraffinic carbon versus carbon monoxide, fall and summer periods.

differ almost by a factor of 2 between the fall and summer periods. These ratios can be interpreted as indicating two different mixes of pollutant sources.

The difference might possibly be a result of atmospheric oxidation of the hydrocarbons. That explanation seems unlikely, however, because of the direction of the differences. Hydrocarbon oxidation occurs more in the summer, which is a time of stagnant midday air, rather than in the fall, which is a time of midday ventilation and air movement. If oxidation were a major factor, the hydrocarbon-to-carbon monoxide ratio would be lower in the summer--the reverse of what has been observed.

A more likely explanation of the difference in ratios can be derived from differences in atmospheric physical properties and atmospheric movements. It is to be noted that the fall measurements taken in the morning and evening showed pollutant concentrations averaging about twice as high as in the summer. This was the result of the air being trapped under a very low-altitude temperature inversion. In the summer, the temperature inversion occurred at a higher altitude, with a resulting larger mixing volume. In the fall, the shallowness of the polluted air layer would restrict the lateral pollution transport. In this case, the pollution at the campus of the California Institute of Technology would be largely auto exhaust from the cars in the nearby streets, and there would be little influence from distant industrial sources or natural sources.

In the summer, the larger mixing volume gives a smaller pollutant concentration than in the fall, but at the same time allows more pollutant transport from a distance. Thus, the summer air at the site could contain, in addition to auto exhaust, evaporated organic materials from sources farther out, including industrial operations, solvent evaporation, and petroleum leaks.

Another factor to be considered is temperature differences, as pointed out recently by Stephens.[14] Midday heat will vaporize organic materials. In the summer, the air is not only warmer and the sun more intense than in the fall, but the air is trapped under a temperature inversion in midday, thus allowing accumulation of the organic vapors. In the fall, the sun and warmth of midday release vapors into a mobile atmosphere that dissipates them quickly.

In summary, this interpretation of the data indicates that in the summer a substantial portion of the organic pollutants comes from sources other than auto exhaust. These infrared data do not give a sufficiently detailed analysis of the hydrocarbon portion of the pollution to identify specific nonautomotive sources of hydrocarbons. Chromatographic analyses are much more informative in that regard.[15,16]

The ratio between ethylene and acetylene is a measure of the degree of photolysis of the polluted air mass. Both pollutants come almost ex-

clusively from auto exhaust and have a fixed ratio if there are no atmospheric transformations. Measurements have shown the average ethylene-to-acetylene ratio in auto exhaust to be approximately one-to-one.[17] A ratio fairly close to this was obtained in the measurements of November 20 to December 1, as shown in Table 2. However, Table 3 illustrates that in the summer, the ratio was frequently much smaller. The ethylene is much more reactive photochemically than the acetylene, with a disappearance rate in smog-chamber experiments many times greater. Thus, the "photochemical age" of the air mass can be judged from this ratio, as discussed, for example, by Stephens and Burleson.[18]

Data from the tables, plotted in Figures 10 and 11, show the variations of pollutant concentrations during the day. The data for July 24 and 25 show an ethylene-to-acetylene ratio about half of the auto exhaust value by midmorning and a ratio in the afternoon only about one-fifth of the auto exhaust value. The indicated high degree of photochemical activity is confirmed by the high values of ozone obtained on those days.

The observation that by noon the ethylene concentration had already fallen as low as one-fifth of the acetylene concentration indicates that fresh ethylene was not coming into the air mass at a high rate. Laboratory measurements with simulated atmospheric conditions have shown the ethylene to have a half-life of several hours. If a large continuous influx of ethylene existed, the steady-state ethylene-to-acetylene ratio should therefore remain much higher than observed. Instead, it appears that the reactive components were transformed early in the day, and they were not replaced.

For comparison, data are shown in Figure 12 for August 9, a summer day on which only a moderate amount of ozone was formed. On this day, the ethylene-to-acetylene ratio remained near one-to-one in the morning and evening and dropped only to about three-to-four in the middle of the day when the photochemical oxidation was at its height. There was also a variation in concentrations during the day.

Pollutant Concentrations as Functions of Time

Carbon monoxide and acetylene, both indicators of auto exhaust, did not vary markedly with time during the smoggy days of July 24 and

25. Nor did they vary markedly during other summer days of moderately high oxidant, such as August 9. The relatively steady value of these pollutants is at variance with a concept of morning and evening auto exhaust peaks. If there was any peaking of the traffic count, it was obscured by the integrating effect of the well-mixed trapped air mass. Probably, the frequently observed morning and evening peaking phenomenon is a result of morning and evening periods of air stagnation separated by a midday period of ventilation. This is the pattern we observed in the fall, when there was no smog. In contrast, on the heavy smog day of July 25, the acetylene and carbon monoxide concentrations peaked at 2:00 p.m. The amounts of carbon monoxide and acetylene on July 24 and 25 were low compared with the amounts frequently reported for urban locations.[16] This emphasizes the important role that the meteorological factors play in the Southern California smog. It is the trapping of the midday air that allows the photochemical reaction products to accumulate.

Three principal reaction products were observed--ozone, formic acid, and peroxyacetyl nitrate. The variations of these with time during the July smog attack are shown in Figure 11. The increase of reaction product concentrations during the morning and early afternoon followed by a falling off in the late afternoon, as seen on July 24 and 25, is typical smog season behavior. This pattern is also shown in the August 9 plots. July 26 seemed to start out as a smoggy day, but by noon the air had gotten moving and cleared out the pollution.

The figures show that on the smoggy days the ethylene concentration went down quickly in the morning. It can be assumed that propylene, butadiene, isobutene, formaldehyde, and other components of the auto exhaust that are more reactive than ethylene decreased in the morning even faster than the ethylene. It is these highly reactive components that are mainly responsible for the morning conversion of nitric oxide to nitrogen dioxide and the start of the ozone buildup. However, there was much more total ozone formed than can be accounted for by the action of the reactive species. It is clear that the less reactive hydrocarbons must

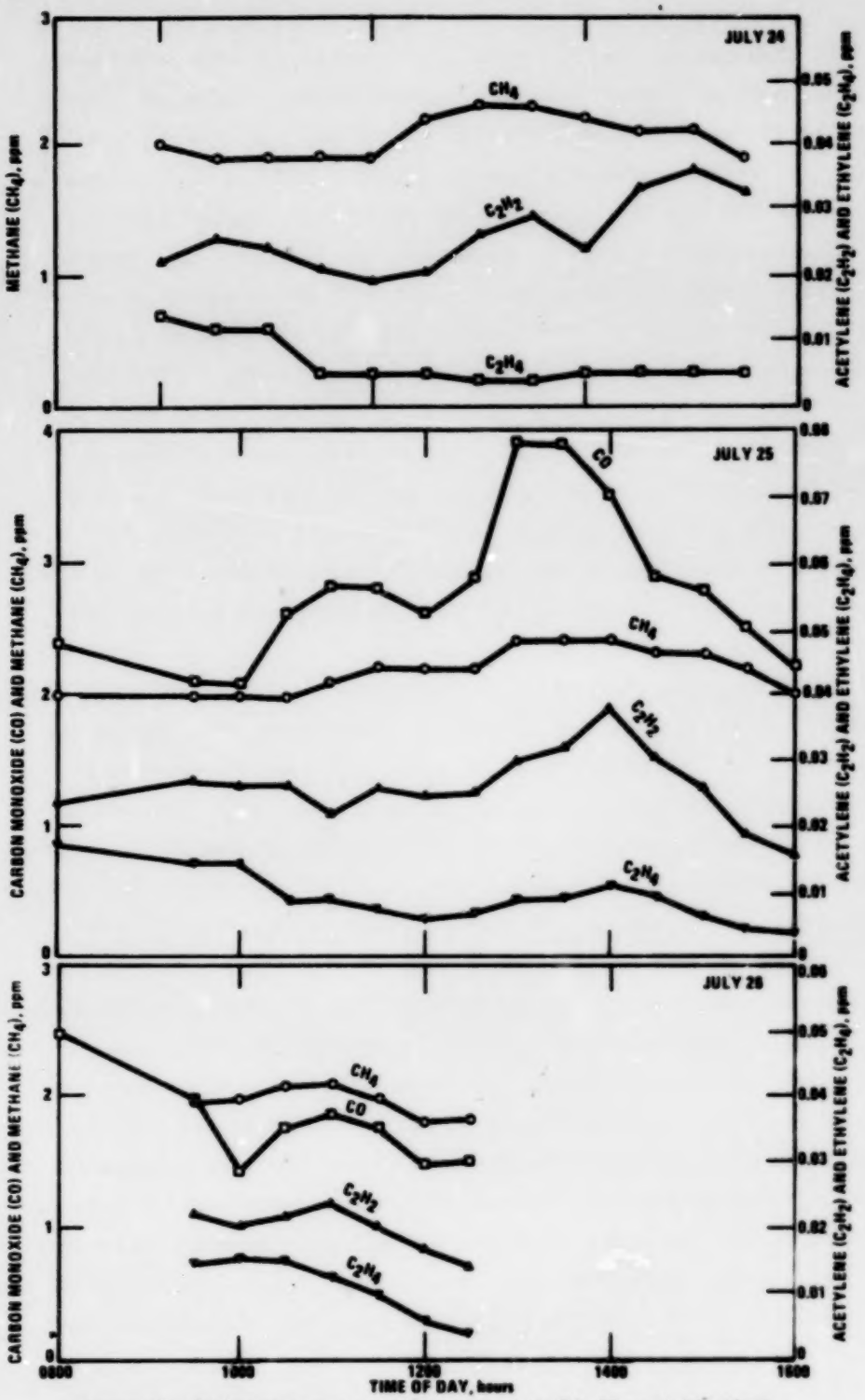

Figure 10. Pollutant concentration plots, July 24, 25, and 26, 1973.

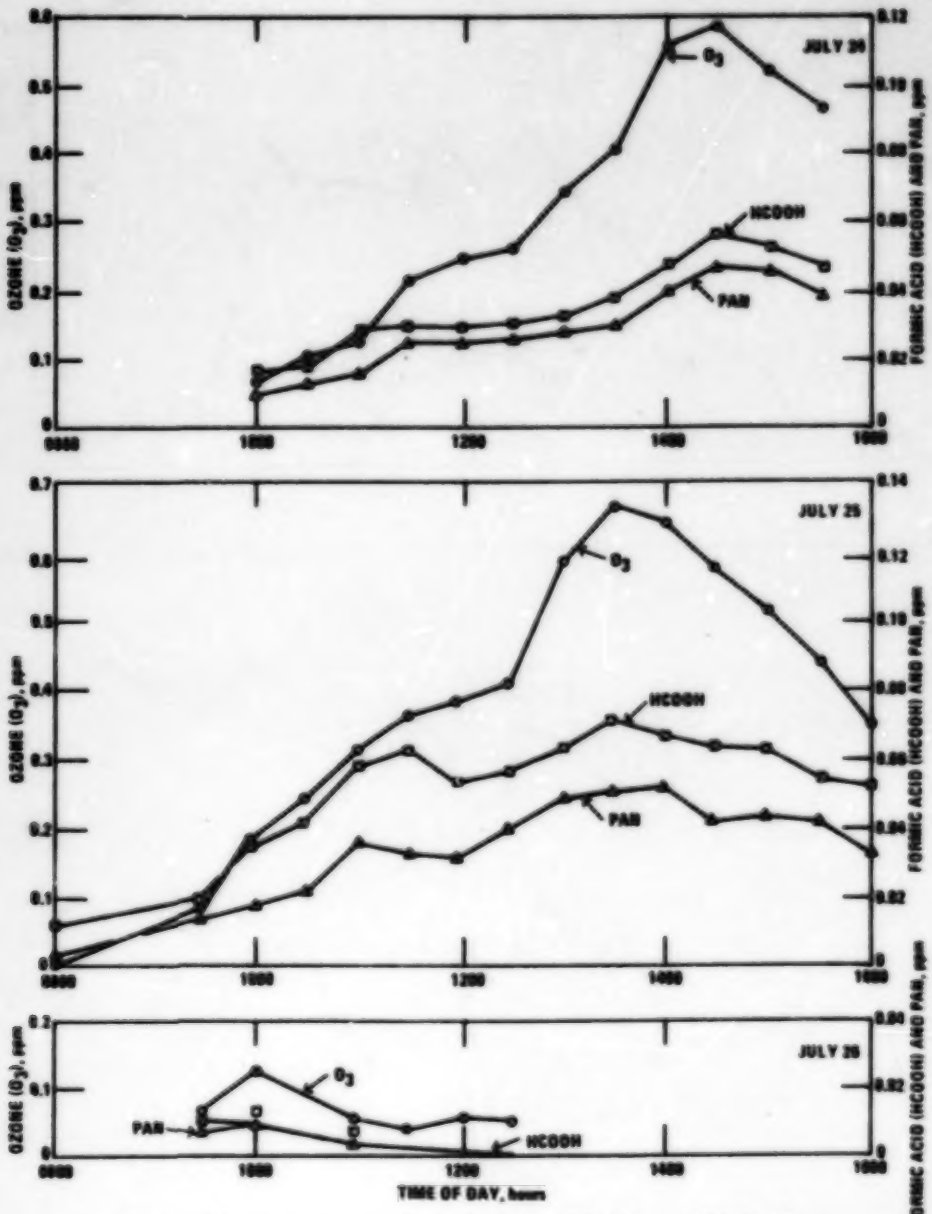

Figure 11. Reaction product plots July 24, 25, and 26, 1973.

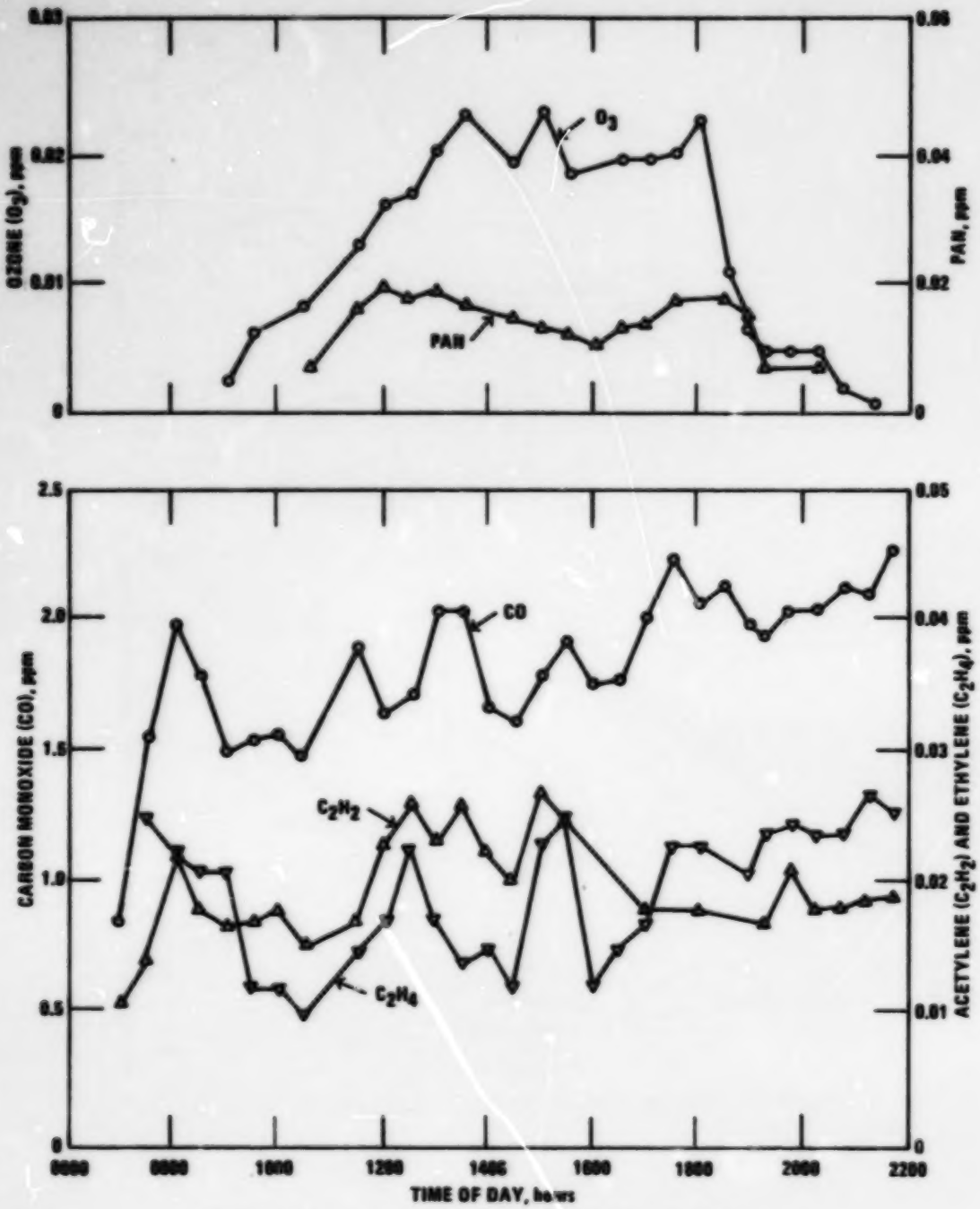

Figure 12. Pollutant and product plots for August 9, 1973.

also be contributing to the ozone buildup. This will be further discussed in connection with the material balance.

Individual Compounds

Acetylene--Acetylene is probably the best indicator compound for the presence of auto exhaust pollution in the atmosphere. No major sources of acetylene other than the internal combustion engine are normally present. Laboratory studies have shown acetylene to be highly resistant to atmospheric oxidation. Its half-life in the atmosphere is probably many days. The compound thus serves as a reference against which to measure the extent of reaction of other species.

The acetylene absorption band at 730 cm^{-1} (Figures 6 and 7) is one of the strongest known, so that small amounts can be measured reliably.

Ammonia--Ammonia is assigned a prominent role in fine particle formation in the atmosphere. Ammonium sulfates and nitrates are major constituents of atmospheric aerosol, as shown, for example, in the reports by Gordon and Bryan and by Charleson et al.[19,20] Decaying vegetation is regarded as the principal source of atmospheric ammonia. Georgii reported about 20 ppb of ammonia in the air at Frankfurt, Germany, but only about 6 ppb in air coming into Europe from the Atlantic Ocean.[21]

The infrared absorption spectrum of ammonia is undoubtedly one of the best indicators of the presence or absence of the compound. The ammonia bands at 930 and 967 cm^{-1} are strong and distinctive. Furthermore, there is very little interference at these wavelengths from water vapor or from other pollutants. We have seen these infrared bands in the spectrum of air at Durham, North Carolina, indicating an ammonia level of about 20 ppb.

Figure 13 shows the 1:00 p.m. spectrum from July 25 as it actually appeared and as it would have appeared if ammonia were present at concentrations of 10 or 40 ppb. Even at 10 ppb, the expected absorption features are several times larger than the noise level in the spectrum. Examination of all of the several hundred spectra recorded in the fall and summer observation periods has failed to show any indication of absorption at the principal ammonia band at 967 cm^{-1}. For many of the spectra, the noise level corresponds to about 5 ppb of ammonia. The indicated low

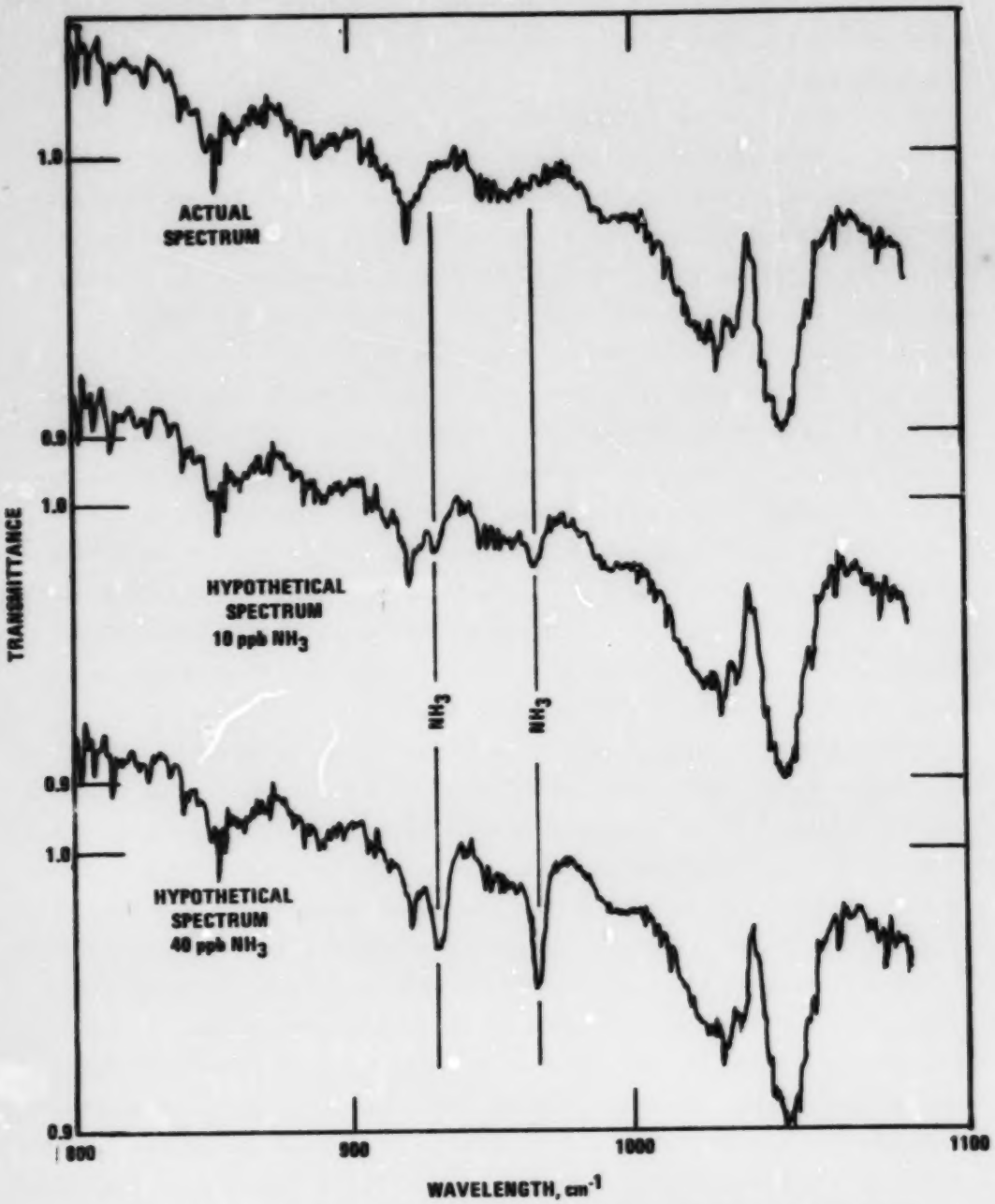

Figure 13. Atmospheric spectrum, July 24, 1973, 1:00 p.m., showing absence of ammonia (NH_3) by comparison with hypothetical spectra for atmospheres containing ammonia.

concentration of gaseous ammonia is understandable in the light of several factors: (1) The amount of decaying vegetation and other organic matter per square kilometer in the Los Angeles area is smaller than in most places where ammonia has been detected. (2) Air coming in from the Pacific Ocean would be expected to be relatively low in ammonia content. (3) Nitrate and sulfate formation in the Los Angeles atmosphere will consume gaseous ammonia.

Carbon Monoxide--The carbon monoxide spectrum occurs with little interference from other compounds. The principal uncertainties of the carbon monoxide measurement come from variations in its apparent absorption coefficient, as previously discussed. The amounts of carbon monoxide detected were smaller than customarily seen in center-city monitoring stations, but were comparable to the amounts measured in outlying areas, such as Riverside.[22] The use of carbon monoxide as an indicator of the air stagnation has been discussed. Carbon monoxide is a comparatively inert compound in the air, with a half-life of several months. Recent studies of carbon monoxide oxidation have outlined the removal paths for carbon monoxide in the air and are important to an understanding of overall atmospheric chemistry.[23] However, it is still generally concluded that carbon monoxide does not significantly influence the short-term atmospheric photochemistry of urban areas.

Ethylene--Much emphasis has been placed on the detection or nondetection of ethylene, and our conclusions as to the low rate of air turnover and high degree of hydrocarbon reaction on smoggy days have largely been based on ethylene measurements. The compound is easily enough measured in the spectrum. Its band at 950 cm^{-1} is strong and sharp, and its spectrum does not suffer serious interference from other atmospheric constituents. Figure 7 shows an ethylene value of 0.009 ppm. Spectra obtained earlier in the summer mornings and in the fall mornings and evenings showed the ethylene band stronger, with a maximum of 0.098 ppm.

Formaldehyde--Formaldehyde is detectable by its characteristic spectral structure in the region 2700 to 2900 cm^{-1}. All the spectra obtained in this study were examined carefully for these spectral lines,

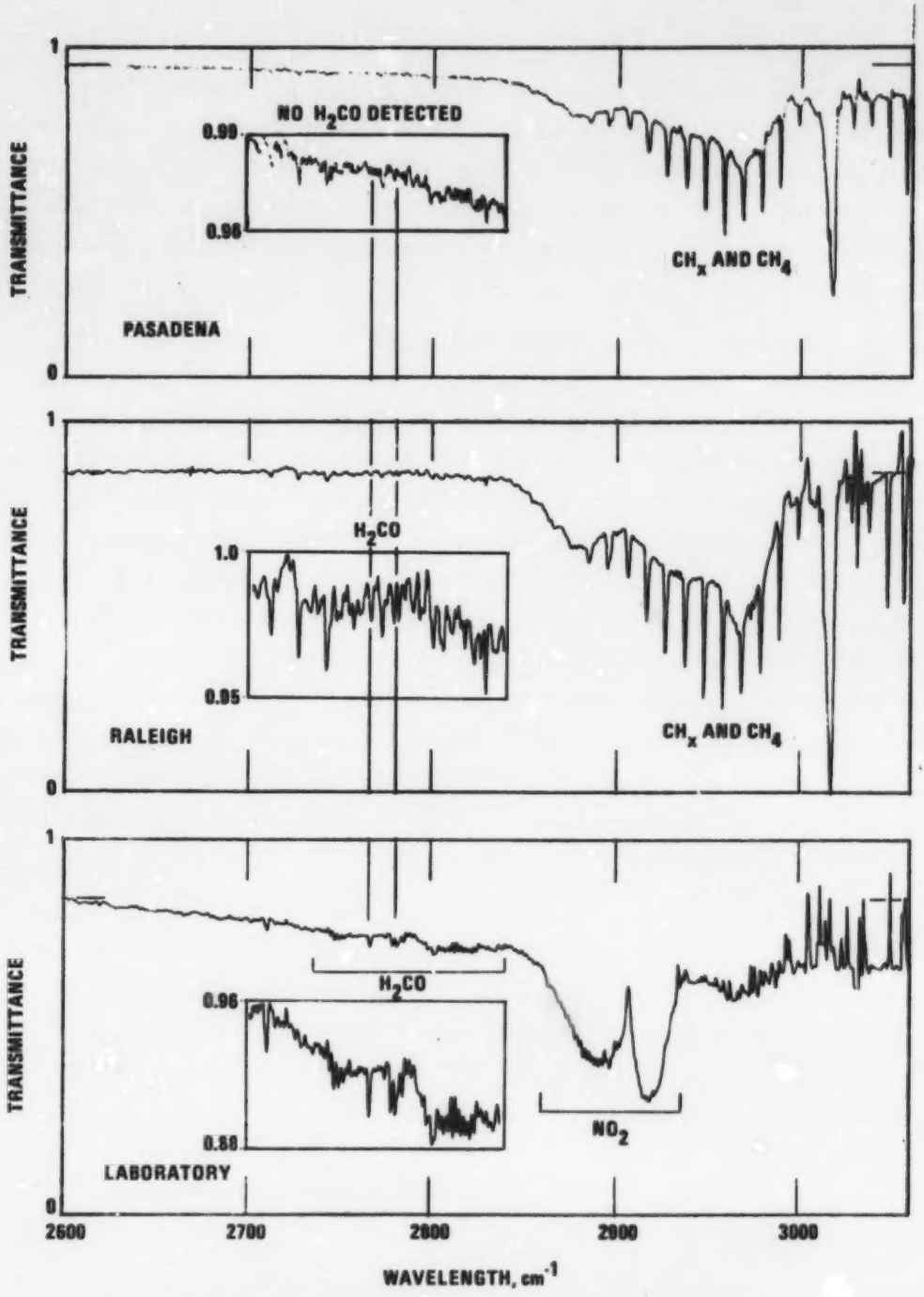

Figure 14. Formaldehyde (H_2CO) response: contrast between Pasadena site, where formaldehyde was not detected, ambient air in Raleigh, N.C., and auto exhaust in laboratory air.

but no lines were found. The detection limit for formaldehyde was approximately 15 ppb in the fall 1972 period and about 30 ppb in the summer 1973 period. The difference is attributed to a somewhat better optical alignment in the fall measurements, which gave a better signal-to-noise ratio.

Although we were surprised at not seeing formaldehyde, we do not believe this to be an anomalous aspect of our results. In the fall period of observation, there was little photochemical activity, so that the only significant source of formaldehyde was its direct emission in auto exhaust. For comparison, we have obtained the absorption spectrum of Raleigh, North Carolina, morning air in the midst of rush-hour traffic. That spectrum did show a trace of formaldehyde vapor but also showed carbon monoxide and hydrocarbon levels two or three times greater than the maximum seen at the Pasadena site. We also obtained the spectrum of air containing a small amount of auto exhaust from a laboratory-operated car equipped with a catalytic muffler. The latter spectrum clearly showed formaldehyde bands along with a large absorption due to nitrogen dioxide. The Raleigh spectrum and the laboratory spectrum are compared in Figure 14 with one of the best of the Pasadena spectra. The formaldehyde is clearly detectable in the laboratory sample at 80 ppb. In the Raleigh air, it is detectable at about 40 ppb. In the Pasadena sample, it is not detectable. It should be noted that the scale-expanded fine structure is similar in the Pasadena and Raleigh samples, except for the formaldehyde bands. This nonformaldehyde fine structure is mainly due to weak lines of methane. If the aldehyde had the same ratio to hydrocarbon in both the Raleigh and Pasadena air samples, it probably was present in the Pasadena air at about 0.015 ppb.

In the summer, more formaldehyde is produced by the photochemical oxidation of hydrocarbons than is emitted directly into the air. Ethylene oxidation is probably the largest single source. However, the aldehyde formed in the air would be further oxidized to formic acid, carbon monoxide, carbon dioxide, and water. In view of the indicated advanced state of oxidation of the polluted air samples on the smoggy days, it is understandable that formaldehyde was not detected.

Formic Acid--The presence of formic acid is revealed by its absorption band centered at 1105 cm^{-1}. This is a fairly strong band that has a distinctive shape and falls in a spectral region where water vapor interference is not great. This band has allowed the infrared detection of formic acid at levels between 10 and 70 ppb.

The detection of formic acid is illustrated in Figure 15. The top curve is a laboratory spectrum of the formic acid and ozone produced by 30 minutes of ultraviolet irradiation of 20 ppm of formaldehyde and 0.5 ppm of nitrogen dioxide in air. The infrared path was 170 meters. Below are seven spectra of the Pasadena air recorded on July 25, 1973, and one recorded on July 26. The spectra show the appearance, growth, and decay of three bands: the ozone band at 1050 cm^{-1}, the formic acid band with absorption peak at 1105 cm^{-1}, and the peroxyacetyl nitrate band at 1165 cm^{-1}. In the 9:30 spectrum at the top, the water bands have been fully cancelled and a very small amount of formic acid appears. The 10:30 spectrum shows more formic acid and a slight undercompensation of the water lines. The 11:30 and 12:30 spectra show an overcompensation of the water lines, which drives them upwards in the ratio plot and clearly reveals the downward-directed formic acid peak. The 1:30 and 2:30 spectra show undercompensation of water, with formic acid still present. The July 26 9:30 a.m. spectrum shows a good water balance, a trace of ozone, and no obvious absorption due to formic acid or peroxyacetyl nitrate. From a scale-expanded plot of this same spectrum, we estimated 8 ppb of formic acid and peroxyacetyl nitrate and 60 ppb of ozone.

The formic acid band appears to lie on top of a weak background of absorption by other species. This caused some difficulty in determining the amount of formic acid, but an attempt was made to minimize the error by measuring only the depth of sharp downward peak.

As Figure 11 has shown, the formic acid concentrations were sightly higher than the peroxyacetyl nitrate concentrations. This means that except for ozone, formic acid is present in the highest concentration of any reaction product seen in these samples of polluted air. Carbon dioxide, carbon monoxide, and water are also products, but they meld into the background and are not measurable.

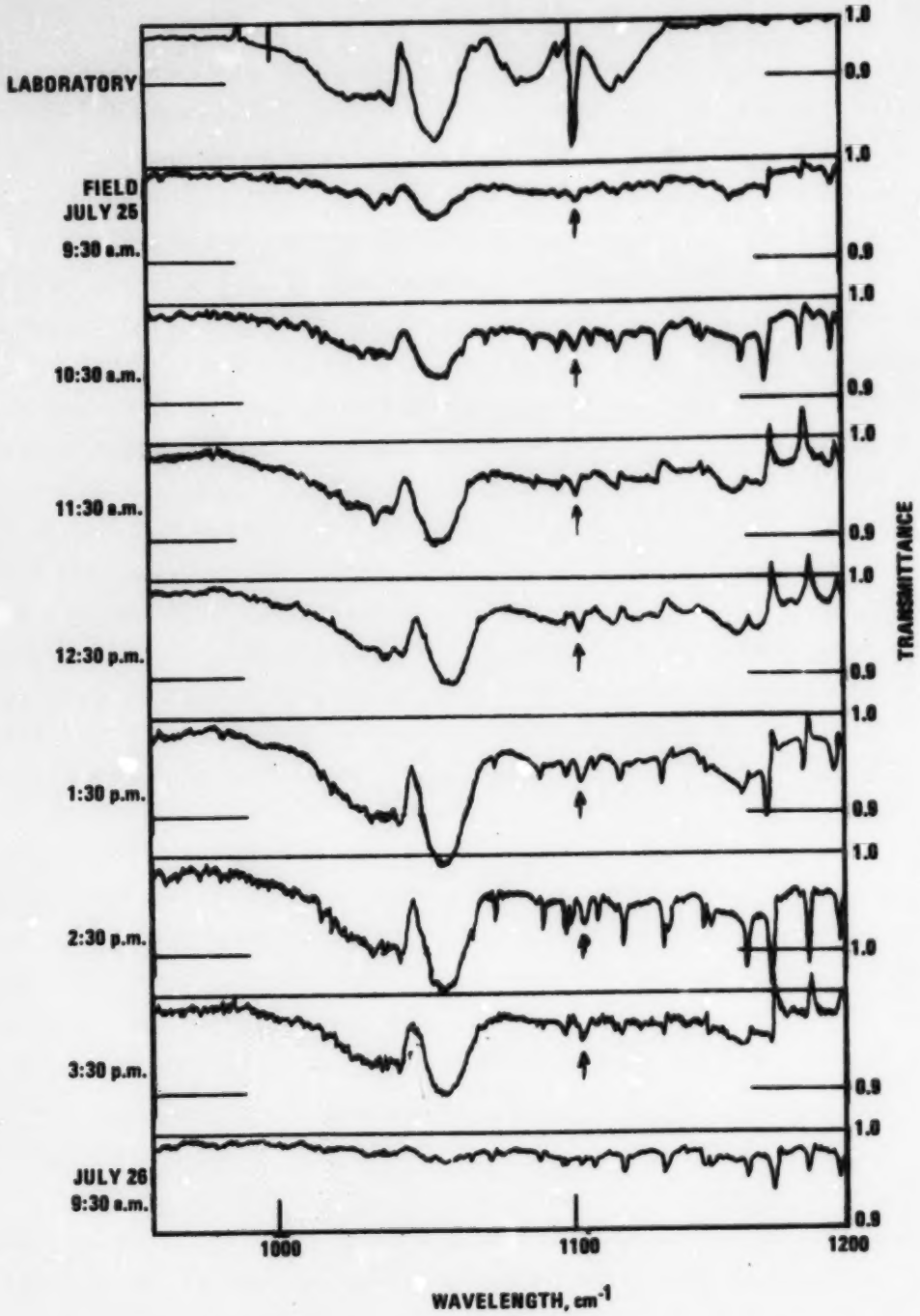

Figure 15. Detection of formic acid (band indicated by arrow).

Laboratory photooxidation studies using the infrared technique for analysis have many times shown the formation of formic acid.[1,2] The acid is a major product of the photooxidation of formaldehyde.[24] Thus, there has always been reason to suspect the acid to be present in the polluted air. However, we believe this to be the first time it has been conclusively identified and measured. In 1955, it was reported that formic acid had been measured in the Los Angeles air at concentrations up to 0.41 ppm.[25] The method used involved the reduction of formic acid to formaldehyde, followed by the reaction of the formaldehyde with chromatropic acid to yield a colored complex. We suspect the method to have been subject to error because the amounts of formic acid reported were about a factor of 5 or 10 greater than the amounts now detected by the infrared method. There is no reason to assume that the composition of the atmosphere is Los Angeles has changed so substantially in the past 20 years. Other indexes of pollution, such as carbon monoxide, ozone, and total hydrocarbons, have not shown such substantial changes. It is interesting to note that Leighton's 1961 summary of the state of knowledge of atmospheric photochemistry[26] did not give any significant consideration to formic acid as a product.

Stability is the reason that there is more acid than aldehyde in the air. The aldehydes are precursors of the acids and have a relatively short lifetime in the sunlit atmosphere. The acids, especially formic acid, represent a stopping place in the sequences of photochemical reactions. Thus, our observations are consonant with the current measurements that are showing organic acids to be constituents of the fine particles in the air.

Halogenated Compounds--The fluorinated and chlorinated hydrocarbons all have strong absorption bands in the frequency region of 700 to 1360 cm^{-1}. The greater the molecular symmetry, the more likely that the bands will have a characteristic shape, and the more sensitive the infrared detection. Thus, we identify carbon tetrachloride by its strong band at 792 cm^{-1} and Freon 12 by its strong band at 921 cm^{-1}. Trichloroethylene and Freon 11 both absorb near 850 cm^{-1} and are undoubtedly contributors to the persistent absorption band at that frequency. In no cases were the de-

tected amounts of a halogenated compound greater than a few parts per billion. The concentrations did not appear to change in any regular pattern. Because of their inertness, the compounds will accumulate in a sluggish urban atmosphere, just as they are accumulating in the atmosphere on the global scale.

Hydrocarbons--In addition to the selected bands of individual light hydrocarbons such as methane, acetylene, and ethylene, the spectra show the combined band at 2970 cm^{-1} due to C-H stretching vibrations in many hydrocarbons. As noted earlier, the band does not include methane or the ring carbons in aromatics. Thus in designating the band as CH_x, the subscript x means two or three hydrogens, but not one or four. The band is useful as a general indicator of the level of hydrocarbon pollution, as has been previously discussed.

Hydrogen Peroxide--It is logical to expect some hydrogen peroxide to be present in the smog along with the other oxidants. The peroxide has been seen as a product in laboratory photooxidations. In addition, it has been measured by Gay and Bufalini in the air in New York City and in Riverside, California. They used the chemical method developed by Cohen and Purcell, in which titanium IV and 8-quinolinol react with the hydrogen peroxide to form a colored complex. They observed that hydrogen peroxide increased in the afternoon in a pattern similar to the ozone build-up, but at concentrations only about one-fifth as great.[26] If the hydrogen peroxide were present at one-fifth the ozone concentration in the Pasadena air on July 24 and 25, it should appear in the spectra.

A reference spectrum of hydrogen peroxide obtained under low resolution is shown in Figure 16. Water bands are seen on the high-frequency side. In the laboratory, we have measured the maximum absorption coefficient of this hydrogen peroxide band to be 9 ± 3 atm^{-1} cm^{-1}, indicating a fairly strong band, similar to the accessible bands of ozone and formaldehyde (Table 1). When the atmospheric spectrum is recorded over a 417-meter path, water and methane both absorb strongly in the same region as the peroxide, and it is difficult to detect the peroxide absorption if it is only at a few percent. One can say from

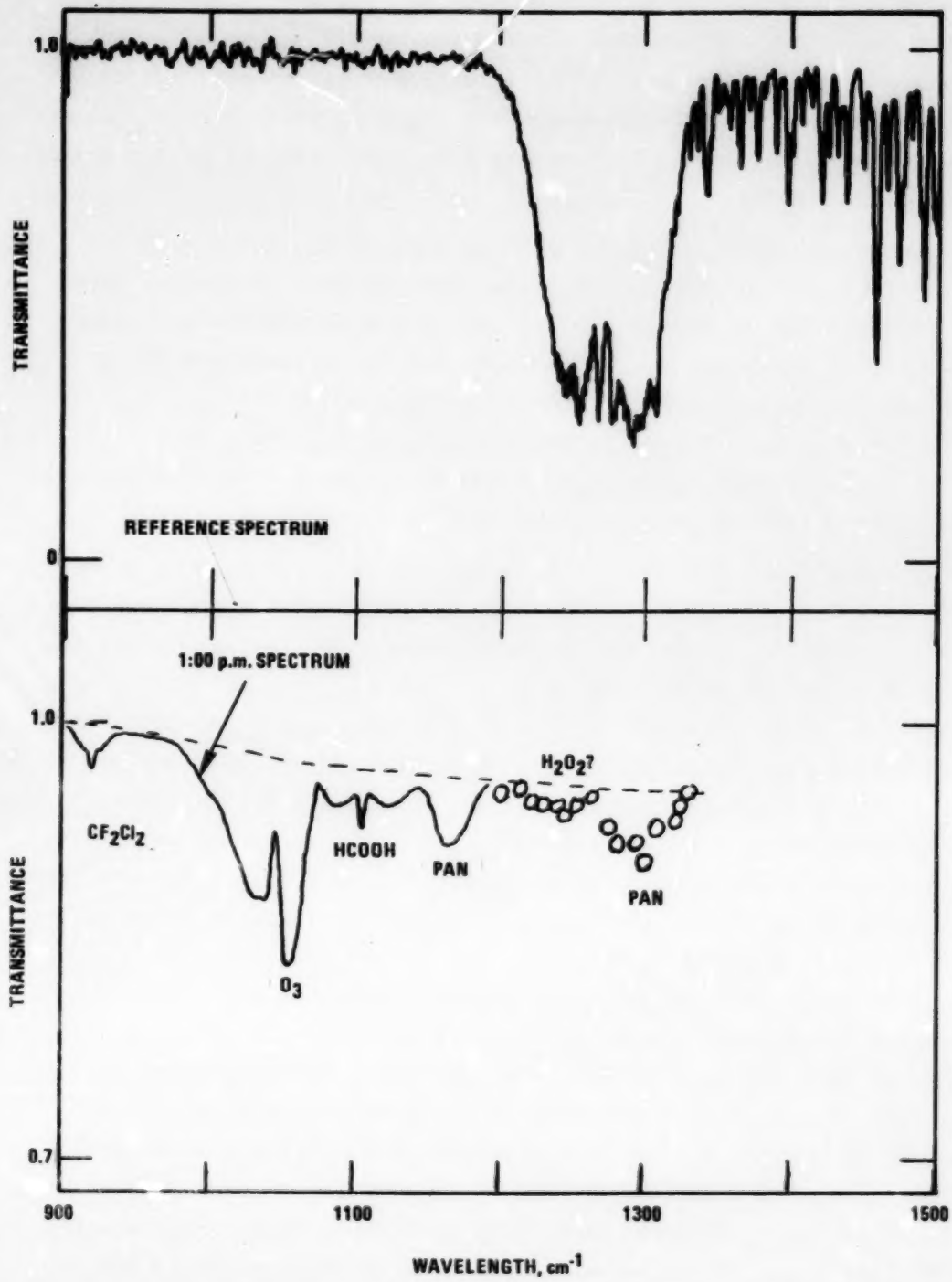

Figure 16. Ratio spectrum showing possible presence of hydrogen peroxide (H_2O_2). Reference spectrum shows 5 ppm H_2O_2 in 1-atm tank air at a path length of 295 meters.

inspection of the ratio spectra, such as in Figure 7, that the peroxide was not present at concentrations of 100 ppb or higher; we wish to go to a lower detection limit than this.

In order to extract any possible hydrogen peroxide absorption from the data, we have carefully compared the single-beam plot of 9:30 a.m. on July 25 with each of the single-beam plots of 1:00 p.m. and 1:30 p.m. on the same day. The spectra were superimposed so that they matched at about 1200 cm^{-1}, and then the ordinates were compared at all the points between the water lines, from 1200 to 1360 cm^{-1}. In each case, this gave us 17 points on a low-resolution ratio plot, showing changes in absorption that occurred between morning and afternoon. The average of the resultant two ratio plots is shown in Figure 16, lower half. The appearance of the peroxyacetyl nitrate absorption band, which we know must be present at about 1300 cm^{-1}, assures us that the ordinate comparison technique is giving a valid answer. From the strength of the 1160-cm^{-1} peroxyacetyl nitrate band, we know that nearly all of the 1300-cm^{-1} band must be due to peroxyacetyl nitrate. The remaining absorption in the figure may be ascribed to hydrogen peroxide. The absorption band depth appears to be about 2 percent, corresponding to about 0.070 ppm hydrogen peroxide. This identification is by no means totally convincing, but at least one might say that the spectrum indicates the possible presence of hydrogen peroxide, not at one-fifth the concentration of the ozone, but perhaps at one-tenth.

Methane--Methane shows in both the high-frequency and low-frequency portions of the spectrum. It was always present at concentrations between 1.8 and 2.8 ppm. The methane is not primarily automotive in origin, and as shown in Figure 10, it does not closely follow the concentration variations of carbon monoxide and acetylene. The most probable source of methane is natural gas.[18,22] It should be noted that the Raleigh air spectrum of Figure 14 shows a higher methane concentration than the Pasadena spectrum.

Methanol--Methanol, revealed by its band centered at 1032 cm^{-1}, appeared in the spectrum occasionally and apparently at random. The maximum amount

detected was about 0.10 ppm, but usually the amount was near or below our detection limit of 0.008 ppm. Consider, for example, the spectra in Figure 15. The 9:30 a.m. spectrum shows 0.013 ppm; the 10:30 spectrum shows none, and the 11:30 a.m. spectrum shows 0.017 ppm; then for the rest of the day the methanol was again below the detection limit. One of the clearest methanol spectra is reproduced in Figure 17. In this

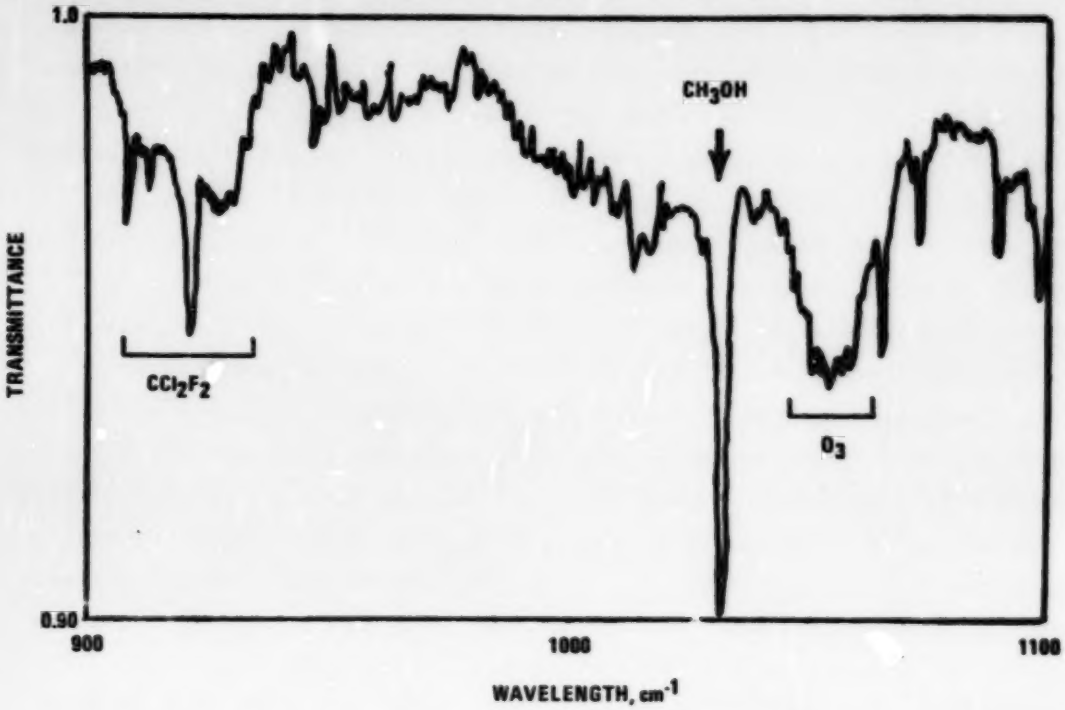

Figure 17. Detection of 0.10 ppm methanol (CH_3OH) and 0.021 ppm Freon 12 (CCl_2F_2); 11:00 a.m., August 23, 1973. Methanol band superimposed on A band due to 0.075 ppm ozone.

case, the amount was 0.10 ppm. The band is somewhat distorted by an overlapping band of 0.075 ppm of ozone. Also shown in the figure is a band due to 0.021 ppm of Freon 12. The random appearances of methanol in our spectra could have resulted from dumping of this solvent somewhere, either in industrial operations, or in some type of activity on the campus. Clearly, methanol is not a photochemical reaction product.

Methyl Nitrate--A laboratory photooxidation of hydrocarbon and nitrogen oxides in air carried out with reactant concentration of one

part per thousand will yield alkyl nitrate as the major nitrogen-containing product. When the reaction is conducted with concentrations of 10 ppm, a mixture of alkyl nitrate and peroxyacetyl nitrate will be formed. At concentrations of 1 ppm, the product is nearly all peroxyactyl nitrate. Thus, we do not expect to find alkyl nitrates in the smog, and the spectra confirm this expectation. The strong methyl nitrate bands at 853, 1018, and 1290 cm^{-1} do not show in any of the spectra. We estimate our detectability limit to have been 0.010 ppm.

Nitric Acid--Evidence of the presence of nitric acid vapor in the air was searched for, but none was found. The spectra place an upper limit of approximately 10 ppb on the level of nitric acid vapor that might have been present but not detected during the period of observation.

The acid has been detected in the upper atmosphere by means of its spectrum, but it has never been detected near the earth's surface. Knowledge of the level of nitric acid present in the lower atmosphere is necessary for understanding the fate of the nitrogen oxides and the mechanics of formation of the nitrate found in the aerosols.

It is known that the acid is formed by the interaction of nitrogen dioxide and ozone:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \rightarrow N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

We have followed these reactions in the laboratory by observing the infrared spectra of the reactants and products. The rate of conversion of N_2O_5 to HNO_3 depends on the amount of water vapor in the system. It appears that the conversion takes place not in the gas phase but at the surface of droplets or on the vessel walls. Nitric acid appears as a gas, but not with the uniform rate that would indicate a homogeneous gas-phase reaction. After an induction time, the acid appears in a surge that is accompanied by the formation of many fine particles in the mixture.

After being formed in the condensed phase, the nitric acid evaporates.

Other possible nitric acid-forming reactions may include nitrogen trioxide abstracting hydrogen from water or hydrocarbons, and nitrogen dioxide combining with hydroxyl radicals. The NO_2--OH combination may be the source of nitric acid vapor in the upper atmosphere, but at ground level such free radical reactions would appear to be a minor source of HNO_3 compared to the NO_2--O_3 interaction.

The nitric acid absorption band most sensitive for atmospheric analysis is centered at about 880 cm^{-1}. At this frequency, water vapor interference is not serious. There are two distinctive "spikes" in the band, located at 879 and 896 cm^{-1}. These features would have revealed the presence of nitric acid with a sensitivity down to approximately 10 ppb.

Figure 18 shows the spectrum from July 25, 1973, 12 noon. The actual spectrum is drawn in the upper part of the figure. Many trace moleculer were detected, as indicated, but there is no evidence of nitric acid. The calculated concentrations of detected species illustrate the detection sensitivity: carbon tetrachloride, 3 ppb; Freon 12, 8 ppb; ethylene, 6 ppb; methanol, 14 ppb; formic acid, 55 ppb; and peroxyacetyl nitrate, 35 ppb. The middle and lower spectra in the figure show the upper spectrum redrawn with added bands of 20 and 100 ppb of nitric acid. We believe the absorption peaks would have been discernible even at nitric acid concentrations as low as 10 ppb. No peaks were seen in any of the several hundred spectra recorded.

Nitrogen Pentoxide--Nitrogen pentoxide is formed in the reaction of nitrogen dioxide and ozone. It hydrolyzes to yield nitric acid. We expect this hydrolysis to take place primarily at the surface of aqueous fine particles, but no measurements or other experimental data on which to base predictions of the rate of hydrolysis were available. All we can say is that a hydrolysis half-life on the order of an hour or more should allow the nitrogen pentoxide to remain in the gaseous state long enough to develop a detectable concentration. Actually, none of the spectra shows the strong nitrogen pentoxide bands at 745 and 1245 cm^{-1}.

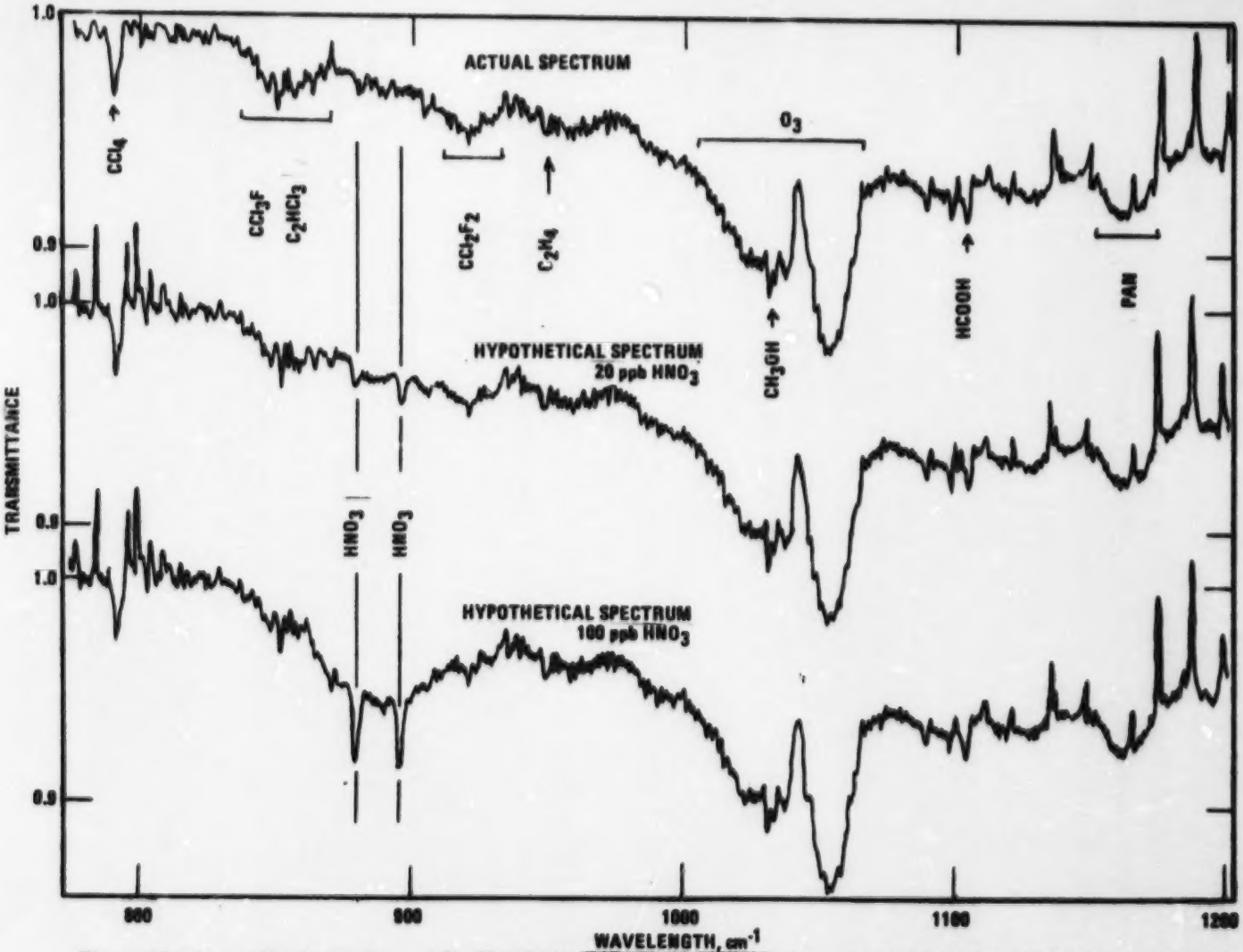

Figure 18. Atmospheric spectrum, July 25, 1973, 12:00 noon, showing absence of nitric acid (HNO_3) by comparison with hypothetical spectra for atmospheres containing nitric acid.

We estimate the detection limit to have been 0.010 ppm.

Nitrous Oxide--Nitrous oxide is an inert constituent of the atmosphere, uniformly distributed. Although it is an oxide of nitrogen, it takes no part in the atmospheric chemistry. The only reason that it is mentioned is that it does appear in the spectra at about 2200 cm^{-1}. The atmospheric concentration of the nitrous oxide is a constant 0.25 ppm, and its bands, along with the bands of carbon dioxide and water, are a permanent part of the infrared background.

Ozone--The prominent band centered at 1050 cm^{-1} gives an accurate measure of ozone, as shown in the figures. Occasionally, a small amount of methanol absorption was seen superimposed on the ozone band, but the amount of methanol could be judged from the band at 1033 cm^{-1}, and a correction could be made. The ozone went through the typical photochemical cycle, as shown in Figure 11, with the highest value being the 680 ppb observed at 1:30 p.m. on July 25, 1973. This unusually high level of photochemical oxidant will be discussed further in the section on material balance.

Peroxyacetyl Nitrate--Peroxyacetyl nitrate is seen most easily by its band at 1165 cm^{-1}, as shown in many of the spectra. Its concentration was very low at night and in the early morning. During the day, it built up to a maximum and then declined in a pattern similar to the pattern of ozone and formic acid concentrations, as shown in Figure 11. Peroxyacetyl nitrate is a strong oxidizing agent, and it is thermally stable in the gaseous state. It readily reacts at surfaces, damaging plants and irritating the eyes. Its reactions with other gaseous pollutants have not been studied extensively, but it is reasonable to assume that such reactions do take place, especially in the case of nitric oxide. Details on the properties and occurrence of peroxyacetyl nitrate in the atmosphere have been given by Stephens.[27]

Material Balance Considerations

The high acetylene-to-ethylene ratio observed on July 24 and 25 leads one to suspect that the average irradiation time for pollutants in the air mass was at least several hours. A more accurate estimate of the rate of air exchange on those days can be made by considering the acetylene and ethylene

to be components in a well-stirred flow reactor. The following assumptions are made: acetylene is nonreactive; ethylene, (E), has a first-order reaction rate: $-d(E)/dt = k(E)$; and, for daytime conditions of high ozone and high photochemical activity, the ethylene half-life is 2 hours. This half-life was derived from the slopes of the ethylene plots of Figure 10 for July 24 and 25 between the hours of 10 and 11 a.m. and is supported by laboratory smog-chamber data. It corresponds to a rate constant, k, of 0.35 hr^{-1}.

Consider the air to be well mixed at the sampling point, with an influx of unreacted polluted air at the ground level, and an outflow of photochemically reacted air at the top of the inversion. Assume the entering ethylene to be at 30 ppb (equal to acetylene), and the outflowing ethylene to be at 6 ppb, as given by our afternoon measurements. At the steady state we have

$$\text{Flow in} - \text{flow out} = \frac{-d(E)}{dt} = k(E)$$

Taking x as the fractional turnover of the air per hour yields:

$$(30x - 6x) = 0.35\ (6)$$

$$x = 0.087\ hr^{-1}$$

The reciprocal of x gives about 11 hours as the time required for one air mass to pass through the reactor.

In view of the low air turnover, it is of interest to estimate the total degree of photochemical oxidation of the air sample. The amounts of acetylene, carbon monoxide, methane, and nonmethane paraffinic hydrocarbons have been given by the infrared measurements. Details of the initial atmospheric composition can be filled in by reference to other work. From measurements at Riverside by Stephens and Burleson[18] and at Los Angeles by Kopczynski *et al.*,[28] the concentrations of hydrocarbon species were estimated and are given in Table 4. Likewise, the amount of nitric oxide introduced into the air mass was estimated through reference to the profile of air contaminant emissions issued by the Los Angeles Air Pollution Control District in January 1971.[29]

The requirement for peroxy radicals, RO_2, is derived from the following considerations. It is firmly established that the O_3 is

Table 4. MATERIALS IN THE PHOTOOXIDATION PROCESS, AVERAGED FOR JULY 24 and 25, 1973

Pollutant	Product maxima	Reactant availability[a]	RO_2 requirement	Maximum RO_2 availability
Ozone	640		640	
Nitric Oxide		350	450	
Peroxy acetyl nitrate	50		100	
			(1190 Total)	
Formic acid	62			
Acetylene		35		
Methyl Acetylene		1		
Olefins				
Ethylene		35		140
Propylene		10		60
1,3-butadiene		1.8		14
1-butene		1.3		10
Isobutene		2.6		21
Trans-2-butene		0.7		6
Cis-2-butene		0.7		6
2-methyl butene-1		1.2		12
Cyclopentene		2.2		22
Trans-2-pentene		1.2		12
2-methyl butene-2		1.3		13
				(316 Total)
Total aromatics, assuming eight carbons per molecule		63		1000
Total nonmethane paraffins, assuming six carbons per molecule		170		2000

[a] Composition of olefin fraction from the September 24, 1968, data of Stephens and Burleson[18]; nitric oxide estimate from Los Angeles Air Pollution Control District Emissions Profile; aromatics and paraffins estimates from Kopczynski et al.[29]

formed from the photolysis of NO_2:

$$NO_2 + NO \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

It is also known that the O_3 reacts very rapidly with the NO to

regenerate NO_2:

$$O_3 + NO \rightarrow O_2 + NO_2$$

The principal role of hydrocarbons in the O_3 buildup is to supply an alternate path for oxidation of NO to NO_2 via peroxy radicals:

$$RO_2 + NO \rightarrow RO + NO_2$$

R may be a saturated or unsaturated hydrocarbon radical and may be partially oxygenated. The RO radical can continue in subsequent reactions. If R is large, the RO radicals can be oxidized to some kind of RO_2 radical one or more additional times.

The O_3 reacts with NO coming into the system, and then with the resulting NO_2 to remove it from the system:

$$O_3 + NO \rightarrow O_2 + NO_2$$

$$O_3 + NO_2 \rightarrow O_2 + NO_3$$

$$NO_3 + NO_2 \rightarrow N_2O_5$$

$$N_2O_5 + H_2O \text{ (at surface)} \rightarrow 2\ HNO_3$$

For each two NO molecules converted to HNO_3, three O_3 molecules are removed, using up to three RO_2 radicals. Formation of a peroxyactyl nitrate molecule uses two RO_2 radicals:

$$NO + RO_2 = NO_2 + RO$$

$$CH_3C(O)OO + NO_2 = CH_3C(O)OONO_2$$

It is assumed that all the NO ends up as HNO_3, nitrate salts, or peroxyacetyl nitrate. Overall, the number of reacted RO_2 radicals equals the total of: (1) the number of O_3 molecules accumulated; (2) 1-1/2 times the number of NO molecules that do not go into peroxyacetyl nitrate but disappear from the system, presumably into HNO_3 or nitrate salts; and (3) 2 times the number of peroxyacetyl nitrate molecules formed. Loss of O_3 in reaction with hydrocarbons is not counted because that reaction probably regenerates RO_2 radicals.

The number of RO_2 radicals available from each organic molecule can be estimated. The number actually generated will depend on how

far the oxidation proceeds. Without considering the detailed oxidation mechanism, it can be stated that the number of RO_2 radicals to be derived from each carbon is probably not more than two. A carbon atom that begins as a $-CH_2-$ group and ends as a CO molecule probably serves as the oxygenated carbon in an RO_2 group only once. If the carbon atom ends up as CO_2 or as HCOOH, it may have been through the RO_2 phase twice. Hydroperoxy radicals (HO_2) may also form, but it is not easy to say how frequently. Only a weakly bound hydrogen will be abstracted by O_2 to yield HO_2. The more strongly bound hydrogens can be abstracted by OH, O, and RO, which do not yield HO_2. In summary, therefore, if each carbon atom is assumed to be able to serve twice as the oxygenated carbon in an RO_2 radical, then some CO, HO_2, aliphatic acid, peroxyacetyl nitrate, and CO_2 can be formed. The figures listed in the table under "Maximum RO_2 availability" are just twice the number of carbons for each molecule listed.

The low measured values of ethylene indicate that olefins were nearly all reacted. Let it be assumed, as shown in Table 4, that 316 ppb of the required 1190 ppb of RO_2 came from olefin oxidation. The aromatics as a class are somewhat more reactive than the paraffins, as shown by Kopczynski et al.[28] Since there probably was about twice as much paraffinic materials as aromatic, it seems fair to estimate that the remaining 874 ppb of required RO_2 came half from aromatics and half from paraffins. Overall, a 20 to 30 percent depletion of carbon by oxidation is estimated. This is borne out by the two measurements of C-H absorption in the late afternoon on July 24 and 25. These points, marked on Figure 9, both have slightly higher CO/CH_x ratios than the average.

In summary, the data show a substantial degree of oxidation of the nonmethane hydrocarbon matter in the air on July 24 and 25. Olefins and aldehydes can be assumed to have been nearly completely reacted. The degree of oxidation of other compounds undoubtedly followed their photochemical reactivities. Highly substituted aromatics and branched-chain paraffins were probably fairly well oxidized, and straight chain paraffins, benzene, methane, and

acetylene were probably only slightly oxidized.

The high level of photochemical oxidation at the sampling location in the July 24 and 25 period is demonstrated by a comparison of the ozone-to-hydrocarbon ratios with those shown in the Environmental Protection Agency document Air Quality Criteria for Hydrocarbons, Figure 5-3.[30] That figure shows the measured maximum 1-hour ozone concentrations plotted against average nonmethane hydrocarbon concentrations for the period 6 to 9 a.m. From our measurements on July 24 and 25, we get a 6 to 9 a.m. total nonmethane hydrocarbon concentration of 1.25 ppm. This is derived from our measured nonmethane paraffinic carbon values with a 30 percent increment to correct for the low absorption coefficient of aromatics and small olefins. From Figure 11, we get 0.57 and 0.66 as the maximum 1-hour average ozone concentration. This yields ozone-to-hydrocarbon ratios of 0.45 and 0.53. Each of these ratios is several times higher than the ones shown in the criteria document. There, the three highest ozone values are shown to have been achieved with ozone-to-hydrocarbon ratios of 0.12, 0.11, and 0.13. Two reasons are seen for the abnormally high ratios in the present work: (1) our sampling point was well above the street, in contrast with the street-level measuring points of many monitoring stations; and (2) the 24th and 25th were days of unusually high photochemical activity.

We now consider the fate of the 350 ppb of nitric oxide which must have entered the air mass along with the measured inert pollutants. Since peroxyacetyl nitrate, at 50 ppb, was the only nitrogen-containing compound detected, the remaining 300 ppb of nitric oxide must have ended up either (1) in the particulate matter and gaseous species that were below the detection threshold, or (2) in the vegetation, soil, and other surfaces.

The nitric oxide equivalents of the measured or allowed compounds are easily enough totaled: 50 ppb are in peroxyacetyl nitrate, 10 ppb

might be in nitric acid, 5 ppb might be in alkyl nitrates, and 20 ppb might be in nitrogen pentoxide. Practically no free nitric oxide would exist because of its fast reaction with ozone. If nitric oxide must be absent, then its equilibrium partner, nitrous acid, must also be absent. Let us estimate a 2 ppb maximum for each.

High levels of nitrogen dioxide are also disallowed because of reaction with ozone. An NO_2 level can be calculated from the stirred-flow reactor approximation with the aid of published rate data.

$$\text{Flow in - flow out} = \frac{-d(NO_2)}{dt}$$

The NO_2 is oxidized to N_2O_5 in two steps:

$$NO_2 + O_3 = NO_3 + O_2$$

$$NO_3 + NO_2 = N_2O_5$$

According to data quoted by Leighton,[31] the first reaction determines the rate by being the slower of the two, with a bimolecular rate constant at 25° C somewhere between 0.010 and 0.002 $ppb^{-1}\ hr^{-1}$. Considering that two NO_2 molecules are removed for each O_3 reacted and using an average O_3 concentration of 400 ppb, we have:

$$\text{Flow in - flow out} = 2 \times \begin{Bmatrix} 0.010 \\ \text{to} \\ 0.002 \end{Bmatrix} \times 400 \times (NO_2) = \begin{Bmatrix} 8 \\ \text{to} \\ 16 \end{Bmatrix} \times (NO_2)$$

We now get the flow in and flow out by using the fractional air turnover of 0.087 hr^{-1} previously calculated from the ethylene-to-acetylene ratio:

$$0.087 \times 350 - 0.087 \times (NO_2) = \begin{Bmatrix} 8 \\ \text{to} \\ 16 \end{Bmatrix} \times (NO_2)$$

Hence: Lower estimate of NO_2 = 3.8 ppb

Upper estimate of NO_2 = 19 ppb

The above estimates consider only the reaction of nitrogen dioxide with ozone; reactions with radicals and molecules other than ozone would further reduce the nitrogen dioxide level.

We believe that there is no point in attempting to compare this estimate with measurements of nitrogen dioxide in the July 24 and 25 afternoon air mass, because the measurement methods in use do not give believable answers under afternoon smog conditions. One method which, in our opinion, would give believable answers is the recently developed laser fluorescence method, in which blue laser light is absorbed by the nitrogen dioxide and emitted as red light. This method has been shown to be highly sensitive, proportional to nitrogen dioxide, and free from interference. In an afternoon smog at El Segundo, California, Tucker et al. showed the nitrogen dioxide concentration to be not more than a few parts per billion.[32] We believe that their measurement method would have given a similar answer if applied to the air at our sampling site.

The amount of nitrate in the atmospheric fine particles can only be roughly estimated, but even a liberal estimate cannot account for more than a small part of the total nitric oxide that entered the air. In an intense smog, there might be 200 micrograms of particulate matter per cubic meter. If this were as much as 30 percent nitrate, by weight, it would only be equivalent to about 20 ppb of nitric oxide.

The sum of all the possible amounts of combined nitrogen is equivalent to only about 130 ppb of nitric oxide. Thus, about 220 ppb are not accounted for, and may have been removed at the surface. These conclusions are summarized in Table 5.

If the estimate of 350 ppb of nitrogen oxides (NO_x) obtained from the Los Angeles emission profile was too high, then the missing fraction of nitrogen oxides would be correspondingly smaller. However, even if the estimate was 100 percent too high, we would still have a substantial fraction of nitric oxide not accounted for.

If the nitrogeneous compounds are not present in the air either in gaseous or particulate form, then they must have been removed at the surface. Such removal processes need to be studied further both in the field and in the laboratory.

Table 5. NITROGEN-CONTAINING COMPOUNDS[a]

Compound	Amount detected, ppb	Maximum allowed, ppb nitrogen
Peroxyacetyl nitrate	50	
Alkyl nitrate		5
Nitric oxide		2
Nitrous acid		2
Nitric acid		10
Nitrogen pentoxide		20
Nitrogen dioxide		20
Particulate nitrate		20
Totals	50	79

[a]Nitric oxide entering air mass: 350 ppb.
Nitric oxide not accounted for: 221 ppb.

Future Work

A few improvements in the infrared detection technique used in this work should yield substantial further progress. Although the detection threshold for many pollutants has been reduced to a level near 10 ppb, this is still about a factor of 10 higher than the limits of detection claimed for the method in a previous paper.[7]

One major source of difficulty in this work was the unsatisfactory working environment, which was too shaky, too cramped, and too subject to temperature fluctuations. The remedy for this is simply to set up the optical system in a fully air-conditioned room away from machinery, with ample space for the optical components. This will allow maintenance of proper optical alignment for maximum throughput, minimum spectral

noise, and less shifting of interference fringes. These environmental improvements alone should double or triple the sensitivity.

Another limitation of the present work was the use of imperfect reference air. Carbon dioxide interference was never fully removed in the ratio plots, and nitrous oxide interference was not removed at all. Furthermore, the balance of the water lines in the ratio spectra was not always ideal because of the temperature fluctuations in the working environment. These errors can be significantly reduced in future studies. We recommend that vaporized liquid nitrogen be used in place of tank "zero air." Measured amounts of carbon dioxide and nitrous oxide gases should be carried into the long-path cell with the nitrogen. Humidification can be achieved by the "wet bag" method already developed in the present work.

Finally, it appears that there is still much to be gained in more fully utilizing the capabilities of the Fourier transform spectrometer system. Tape storage of the ratio spectra will allow retrieval and processing at a later time. The plotting of one ratio spectrum against another will reveal small increases or decreases in pollutant concentrations. A much greater number of scans should be added together in recording the spectra, thus raising the signal-to-noise ratio. The use of a copper-doped germanium detector at liquid helium temperature promises two benefits: it will cover the whole spectral region from 300 to 3500 cm^{-1} on each scan, and it will have higher detectivity than the detectors previously used.

REFERENCES

1. Stephens, E.R., P.L. Hanst, R.C. Doerr, and W.E. Scott. Reactions of Nitrogen Dioxide and Organic Compounds in Air. Ind. Eng. Chem. 48:1948, 1956.

2. Stephens, E.R., W.E. Scott, P.L. Hanst, and R.C. Doerr. Recent Developments in the Study of the Organic Chemistry of the Atmosphere. J. Air Pollut. Contr. Assoc. 6:159, 1956.

3. Scott, W. E., E. R. Stephens, P. L. Hanst, and R. C. Doerr. Further Developments in the Chemistry of the Atmosphere. Proc. Amer. Petroleum Inst. 37(III):171, 1957.

4. Stephens, E.R., P.L. Hanst, R.C. Doerr, and W.E. Scott. Auto Exhaust: Composition and Photolysis Products. J. Air Pollut. Contr. Assoc. 8:333, 1959.

5. Tuesday, C.A. The Atmospheric Photooxidation of Trans-Butene-2 and Nitric Oxide. In: Chemical Reactions in the Lower and Upper Atmosphere. New York, Interscience, 1961. p. 15.

6. Huess, J.M. and W.A. Glasson. Hydrocarbon Reactivity and Eye Irritation. Environ. Sci. Technol. 2:1109, 1968.

7. Hanst, P.L., A.S. Lefohn, and B.W. Gay, Jr. Detection of Atmospheric Pollutants at Parts-per-billion Levels by Infrared Spectroscopy. Appl. Spectroscopy. 27:188, 1973.

8. White, J.U. Long Optical Paths of Large Aperture. J. Opt. Soc. Amer. 32:285, 1942.

9. Hanst, P.L. Spectroscopic Methods for Air Pollution Measurement. In: Advances in Environmental Science and Technology, Pitts, J.N. and R.L. Metcalf (ed.). New York, John Wiley and Sons, Inc., 1971. p. 91.

10. Erley, D.S. and B.H. Blake. Infrared Spectra of Gases and Vapors (Vol. II). Dow Chemical Company. Midland, Mich. 1965.

11. Hanst, P.L., E.R. Stephens, W.E. Scott, and R.C. Doerr. Absorptivities for the Infrared Determination of Trace Amounts of Ozone. Anal. Chem. 33:1113, 1961.

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12. Stephens, E.R. Absorptivities for the Infrared Determination of Peroxy Acyl Nitrates. Anal. Chem. 36:928, 1964.

13. Junge, C. and J. Hahn. N_2O Measurements in the North Atlantic. J. Geophys. Res. 76:8143, 1971.

14. Stephens, E.R. Hydrocarbons in Polluted Air. University of California. Riverside, California. Summary Report, Project CAPA-5. June 1973.

15. Stephens, E.R. and F.R. Burleson. Analysis of the Atmosphere for Light Hydrocarbons. J. Air Pollut. Contr. Assoc. 17:147, 1967.

16. Lonneman, W.A., S.L. Kopczynski, P. Darley, and D. Sutterfield. Hydrocarbon Composition in Urban Areas. Environ. Sci. Technol. 8:229, 1974.

17. Neligan, R.E., P.L. Mader, and L.A. Chambers. Exhaust Composition in Relation to Fuel Composition. J. Air Pollut. Contr. Assoc. 11:178, 1961.

18. Stephens, E.R. and F.R. Burleson. Distribution of Light Hydrocarbons in Ambient Air. J. Air Pollut. Contr. Assoc. 19:929, 1969.

19. Gordon, R.J. and R.J. Bryan. Annonium Nitrate in Airborne Particles in Los Angeles. Environ. Sci. Technol. 7:645, 1973.

20. Charleson, R.J., A.H. Vanderpol, D.S. Conert, A.P. Waggoner, and N.C. Alquist. Sulfuric Acid-Ammonium Sulfate Aerosol: Optical Detection in the St. Louis Region. Science. 184:156, 1974.

21. Georgii, H.W. Oxides of Nitrogen and Ammonia in the Atmosphere. J. Geophys. Res. 68:3963, 1963.

22. Stephens, E.R., E.F. Darley, and F.R. Burleson. Sources and Reactivity of Light Hydrocarbons in Ambient Air. Proc. Amer. Petroleum Inst. Division of Refining. 47:466, 1967.

23. Weinstock, B. and H. Niki. Carbon Monoxide Balance in Nature. Science. 176:290, 1972.

24. Hanst, P.L. and J.G. Calvert. The Oxidation of Methyl Radicals at Room Temperature. J. Phys. Chem. 68:71, 1959.

25. Mader, P.P., G. Cann, and L. Palmer. Effects of Polluted Atmospheres on Organic Acid Composition in Plant Tissues. Plant Physiol. 30:318, 1955.

26. Gay, B.W., Jr., and J. J. Bufalini. Hydrogen Peroxide in the Urban Atmosphere. In: Advances in Chemistry Series, No. 113. Washington, D. C. American Chemical Society, 1972. p. 225.

27. Stephens, E.R. The Formation, Reactions, and Properties of Peroxyacyl Nitrates (PANS) in Photochemical Air Pollution. In: Advances in Environmental Science and Technology Vol. 1, Pitts, J.N. and R.L. Metcalf, (ed.). New York, Wiley Interscience, 1969. p. 119.

28. Kopczynski, S.L., W.A. Lonneman, F.D. Sutterfield, and P. E. Darley. Photochemistry of Atmospheric Samples in Los Angeles. Environ. Sci. Technol. 2:132, 1968.

29. Air Quality Profile of Air Contaminant Emissions. Los Angeles County Air Pollution Control District. Los Angeles, Calif. Jan. 1971.

30. Air Quality Criteria for Hydrocarbons. National Air Pollution Control Administration, U. S. Department of Health, Education, and Welfare. Washington, D. C. Publication No. AP-64. March 1970.

31. Leighton, P.A. Photochemistry of Air Pollution. New York, Academic Press, 1961. p. 157.

32. Tucker, A.W., A.B. Peterson, and M. Birnbaum. Fluorescence Determination of Atmospheric NO and NO_2. Applied Optics. 12:2036, 1973.